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OF THE
NATIONAL BUREAU OF STANDARDS

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JOURNAL OF RESEARCH
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U.S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP709

Part of Journal of Research of the National Bureau of Standards, Volume 13, September 1934

OPACITY STANDARDS

By Deane B. Judd

ABSTRACT

Opacity of paper is commonly specified by the contrast-ratio method. According to this method the reflectance of the material backed by a perfectly absorbing surface divided by its reflectance when backed by a highly reflecting material such as magnesium oxide is taken as an index of opacity. Magnesium oxide, itself, is, however, commonly not used as the white backing because of its fragility; nor is the white backing placed in actual contact with the sample. Because of these and other sources of error, opacimeters frequently give erroneous results. Standards of opacity made of permanent material serve to check and to calibrate such instruments. Such standards made of opal glass are described, the theory of their application is given, and results of tests by their use reported. It is found that TAPPI opacity corresponds to a reflectance of white backing in contact with the sample of about 0.89.

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I. INTRODUCTION

The opacity of a sheet of any material (paper, cloth, porcelain, and the like) may be specified by its contrast ratio. Contrast ratio is defined [1] as the apparent reflectance of the material backed by a perfectly absorbing surface divided by its apparent reflectance when backed by magnesium oxide. Because of the fragility of magnesium oxide surfaces, opacimeters for routine determinations are commonly made with white backings other than MgO and sometimes these surfaces are protected by the interposition of an air space, a cover glass, or both. The official method of the Technical Association of

[1] Circular of the Bureau of Standards C63, *Specification of the transparency of paper and tracing cloth*, May 17, 1917.

the Pulp and Paper Industry (the TAPPI method)[2] for the determination of opacity of paper is an example of this practice. The errors which may arise through these deviations from the definition have been discussed for perfectly diffusing, nonabsorbing materials and the theoretical expressions derived were shown to apply closely to a few paper and opal-glass samples.[3]

A standard of opacity made of a permanent material is of use in checking the adjustment of opacimeters. Two sorts of such standards have been prepared. They are (1) solid-opal glass, ground to nearly uniform thickness, one face fire-polished, the other fine-ground, and (2) flashed-opal glass, the flashed face fire-polished, the other face fine-ground. It is the purpose of this paper to describe tests of these standards, to outline the method of checking an opacimeter by their use, and to show the relation of TAPPI opacity to contrast ratio.

II. THEORETICAL RELATIONS

In the interpretation of tests on the standards use is made of three relations derived theoretically from the assumptions (1) that the samples are homogeneous, (2) that both sample and backings reflect light in a perfectly diffuse way, and (3) that the samples are sufficiently thin that no appreciable amount of light is lost through the edges. The following symbols are used:

$R_0 \equiv$ the reflectance of the sample when in contact with a backing of zero reflectance,

$R_1 \equiv$ the reflectance of the sample when in contact with a backing of unit reflectance,

$R_{R'} \equiv$ the reflectance of the sample when in contact with a backing of reflectance, R',

$C \equiv R_0/R_1$, called the ideal contrast ratio,

$C_{.97} \equiv R_0/R_{.97}$, called the true contrast ratio according to the definition which specifies as the white backing magnesium oxide, for which $R'=0.97$,[4]

$C_{R'} \equiv R_0/R_{R'}$, called the measured contrast ratio when the reflectance of the surface or cavity in contact with the back of the sample is R',

$s \equiv$ the number of standard scattering layers required to duplicate the scattering produced by unit thickness of the sample,

$x \equiv$ the thickness of the sample varying from zero up to the thickness for which light escaping through the edges of the sample becomes appreciable,

$R_\infty \equiv$ the reflectivity of the material, that is, the reflectance of the material of the sample in a layer infinitely thick.

[2] No. T425m, obtainable from the association at 122 East 42d Street, New York, N.Y.

[3] D. B. Judd, *Sources of error in measuring opacity of paper by the contrast-ratio method.* BSJ.Research 12, 345 (1934); RP660.

[4] International Critical Tables, 5, 262.

1. MEASURED CONTRAST RATIO AS A FUNCTION OF REFLECTANCE OF WHITE BACKING AND REFLECTANCE OF SAMPLE

$$C_{R'}=\frac{C(1-R'R_0)}{C(1-R')+R'(1-R_0)} \tag{1}$$

This formula may be derived by argument analogous to that used in deriving equation 4 in a previous paper [5] which applies to nonabsorbing samples. For a nonabsorbing sample, $C=R_0$; for this case equation 1 reduces to the previous result. Similar lines of reasoning have been used by Channon, Renwick, and Storr [6] and, still earlier, by Stokes [7] in the derivation of an expression for $R_{R'}$. The expression for $C_{R'}$ for nonabsorbing samples also follows directly from a formula for $R_{R'}$ derived by Kubelka and Munk by independent argument.[8]

2. MEASURED CONTRAST RATIO AS A FUNCTION OF THICKNESS AND SCATTERING POWER OF THIN SAMPLES

$$\left.\begin{aligned} C_{R'}&\equiv R_0/R_{R'} \\ R_{R'}&=\frac{(R'-R_\infty)/R_\infty-R_\infty(R'-1/R_\infty)e^{sx(1/R_\infty-R_\infty)}}{(R'-R_\infty)-(R'-1/R_\infty)e^{sx(1/R_\infty-R_\infty)}} \end{aligned}\right\} \tag{2}$$

The expression for $R_{R'}$ is the one derived by Kubelka and Munk [9] as their equation 5. R_0 is found by setting $R'=0$.

3. MEASURED CONTRAST RATIO AS A FUNCTION OF REFLECTANCE OF THE BLACK BACKING FOR THIN, NONABSORBING SAMPLES

$$R_{R'}/R_1=\frac{C+R'-2R'C}{1-R'C}$$

This formula is derived by argument similar to that used for equation 4 in a previous paper [10]. Since the black-lined cavities used in opacimeters commonly reflect less than 0.002, application of this formula discloses that errors from deviation of the reflectance of the black backing from zero are negligible; for paper samples they are less than 0.001. No further attention will be paid to this source of error.

III. TESTS OF THE STANDARDS

Five solid-opal-glass standards (A1 to A5)[11] and 5 of the flashed-opal standards (B1 to B5) were prepared in the form of rectangles 5 by 20 cm; the thicknesses are about 1.5 mm. The standards were engraved with the identifying marks.

[5] See footnote 3, p 282.
[6] H. J. Channon, F. F. Renwick, and B. V. Storr, *The behavior of scattering media in fully diffused light*, Proc. Roy. Soc., London, [A] **94**, 222 (1918). See their equation 2.
[7] G. G. Stokes, *On the intensity of the light reflected from or transmitted through a pile of plates*, Proc. Roy. Soc., London, **11**, 545 (1860–62). See his equation 6.
[8] P. Kubelka and F. Munk, *Ein beitrag zur optik der farbanstriche*, Z. f. Techn. Phys. **12**, 593 (1931). See their equation 8.
[9] See footnote 8.
[10] See footnote 3, p. 282.
[11] The use of solid-opal glass with fine-ground surfaces for standards of opacity was suggested to the Bureau by J. W. Forrest, of Bausch and Lomb Optical Co. in the summer of 1933.

1. UNIFORMITY

Since the five solid-opal-glass standards were cut from the same sheet it may be expected that thickness is the chief determinant of opacity. This does not apply, of course, to the standards of flashed-opal glass. Accordingly, an attempt was made to correlate opacity with thickness for the solid-opal-glass standards. Two measurements of contrast ratio were made on each of the 10 standards, one measurement applying chiefly to the engraved end, the other chiefly to the end not engraved. Table 1 shows the results of this test.

TABLE 1.—*Uniformity of the standards*

Standard	Engraved end		End not engraved		Standard	Engraved end		End not engraved	
	Thickness	C_w	Thickness	C_w		Thickness	C_w	Thickness	C_w
	mm		*mm*			*mm*		*mm*	
A1	1.52	0.839	1.45	0.837	B1	----	0.477	----	0.490
A2	1.53	.834	1.44	.834	B2	----	.474	----	.467
A3	1.54	.834	1.45	.829	B3	----	.476	----	.471
A4	1.62	.842	1.51	.836	B4	----	.474	----	.478
A5	1.70	.846	1.60	.846	B5	----	.498	----	.508

These values of contrast ratio represent means of 10 settings each; the uncertainty is about 0.004. It may be seen that the variations in opacity from one end of the standards to another indicated by these measurements are scarcely, if at all, significant for the solid-opal-glass standards. The correlation with thickness is suggested but is somewhat masked by experimental error. The variation in opacity from one end to the other of two (B1 and B5) of the flashed-opal standards is significant. It is concluded that the thickness of the diffusing layer of these flashed-opal-glass standards is importantly inconstant and that on the contrary the thickness of the solid-opal-glass standards is not importantly inconstant.

2. CLEANABLENESS OF THE FINE-GROUND SURFACES

As stated before, one face of each standard was left fire-polished; this face is always toward the white backing and is not viewed by the photometer. The other face of each standard is fine-ground. Since there may be a difference between the surface obtained by fine-grinding clear glass and that obtained by fine-grinding opal glass, because of nonhomogeneity of the latter, the two surfaces were tested separately to determine the degree to which they may be cleaned.

The method of test was: (1) Wash thoroughly with soap and water by rubbing with the finger tips, and measure contrast ratio; (2) rub with lampblack and machine oil, wash with soap and water, and measure contrast ratio; (3) repeat process (1); (4) rub with lampblack and machine oil, wash with gasoline, wash with soap and water, and measure contrast ratio.

It was found that the fine-ground surface of clear glass was cleaned by washing with soap and water as far as visual inspection could distinguish: measurement of contrast ratio, however, revealed that an

appreciable amount of lampblack remained. This residual amount was removed by washing both with gasoline and with soap and water.

Visual inspection of the fine-ground surface of opal glass showed that all the washings had failed to remove the lampblack completely, but measurement showed that the washings had succeeded in restoring the original value of contrast ratio. Since soiling with oil and lampblack is regarded as a rather severe test, no further attempt was made to find a more effective cleaning method.

3. APPLICABILITY OF THE FORMULA FOR THIN SAMPLES TO THE STANDARDS

The appreciable thickness (1.5 mm) of the standards might be sufficient to make formulas inapplicable which were derived on the assumption of no loss of light through the edges. Accordingly, measured contrast ratio, $C_{R'}$, was found for standards A2 and A3 using three different white backings, fresh magnesium carbonate ($R'=0.96$), old magnesium carbonate ($R'=0.92$) and cardboard ($R'=0.78$). These values of reflectance were found for nearly diffuse illumination and perpendicular viewing relative to magnesium oxide whose reflectance is taken as 0.97.[12] The reflectance of the solid-opal-glass standards backed by black velvet, R_0, was found in the same way to be 0.71. Measured contrast ratio was determined on the original model designed and used by Priest.[13] The color temperature of the illuminant for measurement of both reflectance and contrast ratio was about 2,400 K. Care was taken to insure that the white backings were within 0.2 mm of the standards over the entire effective area (4 cm diam.). Table 2 gives the values of $C_{R'}$ found in this way and values of $C_{.97}$ found from them by application of formula 1. This application consisted of two stages: First, ideal contrast ratio, C, was found from formula 1 in terms of the known quantities, $C_{R'}$, R_0, and R'; then true contrast ratio, $C_{.97}$, was found for these values of C by substituting $R'=0.97$ directly in the formula.

TABLE 2.—*Measured contrast ratio and true contrast ratio*

	Standard A2		Standard A3	
R'	$C_{R'}$	$C_{.97}$	$C_{R'}$	$C_{.97}$
0.96	0.836	0.832	0.836	0.832
	.835	.831	.838	.834
	.830	.826		
0.92	.856	.834	.851	.829
0.78	.899	.832	.903	.836
	.900	.833		

Since each ratio is uncertain by about 0.004, the differences are not significant, and it may be concluded that the formula for thin samples applies to the solid-opal-glass standards within the experimental uncertainty. For much smaller effective areas, however, the amount of light lost through the edges might be appreciable; each particular condition of illuminating and viewing requires separate study.

[12] See footnote 4, p. 282.
[13] See footnote 1, p. 281

A similar test of the flashed-opal-glass standards showed formula 1 to be inapplicable by amounts exceeding 0.01 over the same range in reflectance, R', of backing. Such a result might have been expected because of the greater loss of light through the clear-glass edges between the flashed-opal back layer and the fine-ground front surface. A satisfactory treatment of these standards was obtained by the assumption that the two scattering layers separated by 1.5 mm would behave essentially like a single scattering layer located 0.5 mm away from the white backing. This latter case is handled by a previously derived approximate formula [14] extended so as to take account of absorption of light by the sample.

4. PERMANENCE

Since these standards have been made up only for a few months, no very conclusive evidence as to the constancy of their opacity is at hand. In 3 months none of the standards has shown any unexplained variations. While glass undergoes some alteration in surface character with time, there seems to be little basis for expecting a significant change in opacity of these standards. Periodic checks are planned as a test of this presumption.

IV. APPLICATION OF THE STANDARDS

Because of several advantages possessed by the solid-opal-glass standards, it is planned for the present to use them to the exclusion of the flashed-opal type. They are more suitable because (1) they are more uniform, (2) their opacity depends less on soiling, (3) the formula for thin samples may be used, (4) their opacities are close to those of the writing and printing papers chiefly tested, and (5) they introduce less chromaticity difference between the two halves of the photometric field.

The general plan of using the opal-glass standards is to issue one of them to the owner of an opacimeter together with values of reflectance for black backing, R_0, and of ideal contrast ratio, C. The recipient measures the standard on his opacimeter and obtains $C_{R'}$. This determines R' for the opacimeter under test according to the relation:

$$R' = \frac{C(1-C_{R'})}{C_{R'}(1-C)+R_0(C-C_{R'})} \tag{4}$$

which follows from formula 1.

If this value of reflectance of the surface or cavity in contact with the back of the sample conforms to the desired definition of opacity, the instrument is reading correctly. This value is 0.97 if true contrast ratio is being used; it is about 0.89, as will appear later, for the TAPPI definition of opacity. If the desired value of R' is not obtained either the operator may adjust the reflectance by suitable means until it reads correctly or he may compute opacity by formula 1 as discussed presently.

[14] See equation 5 in the paper referred to in footnote 3, p. 282.

1. DEPENDENCE ON POSITION OF THE SAMPLE

As just outlined, the use of the standards of opacity may be regarded as an indirect way of determining the reflectance of the surface or cavity in contact with the back surface of the standard. If the sample to be measured is placed so that its back surface occupies the plane previously occupied by the back surface of the standard, the method of calibration described gives the correct value of opacity. In some instruments, however, it is inconvenient to insert samples of varying thickness so that the back surfaces always lie in the same plane. This is the case with the present Bureau of Standards type of instrument; it is a minor defect of design. For these instruments account must be taken of the fact that the standards fill the slot which is only partially filled by the sample holder and thin sample; the result is that the back plane of the sample is 0.5 to 0.7 mm further from the white backing than the back plane of the standard.

In this case the reflectance of the cavity commencing approximately at the central plane of the standard instead of the back plane must be deduced from the opacity measurement of the standard. This is done by application of the approximate formula previously derived for the dependence of $C_{R'}$ on separation from the white backing [15] extended so as to take account of light absorption by the sample. It is found, and checked by experiment, that for this purpose the standard has to be assigned a value lower than the ideal contrast ratio by about 0.02. The remainder of the calibration, whether by adjustment of the instrument or by use of formula 1 is carried out as before. The calibration, however, is somewhat less certain because the position of the sample is imperfectly controlled.

2. DEPENDENCE ON LIGHT-ABSORPTION BY THE SAMPLE

In case it is not possible to adjust the value of R' (by substitution of a new white backing or by adjustment of the separation from the sample), or if it is preferred for other reasons to use formula 1 for computation of opacity, an approximate value of reflectance, R_0, is needed. This value may be estimated with sufficient accuracy for many samples of small light absorption by taking account of the known dependence of R_0 on thickness.

In the previous paper [16] it was assumed that formulas derived for nonabsorbing samples would apply to white paper and a good check was obtained for the samples tested which had $C_{.97}$ less than 0.75. By this assumption the sample in a thick layer would have unit reflectance, and since many kinds of papers have reflectivities of about 0.80, the assumption leads to appreciable error for samples of high opacity though the error is small for samples of lower opacity. A more accurate representation of actual samples regardless of opacity is obtained by taking $R_\infty = 0.80$. Table 3 shows corrections to be subtracted from instrument readings, $C_{R'}$, in order to obtain true contrast ratio, $C_{.97}$, for samples having reflectivities (R_∞) equal to 0.80.

[15] See footnote 14, p. 286.
[16] See footnote 3, p. 282.

TABLE 3.—*Corrections to be subtracted from instrument readings, C_R', to give true contrast ratio, $C_{.97}$, for thin samples of a material having a reflectivity (R_∞) equal to 0.80*

	$(C_R'-C_{.97})$												
C_R'	$R'=0.76$	$R'=0.78$	$R'=0.80$	$R'=0.82$	$R'=0.84$	$R'=0.86$	$R'=0.88$	$R'=0.90$	$R'=0.92$	$R'=0.94$	$R'=0.96$	C_R'
0.00	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.00
.05	.010	.009	.008	.007	.006	.005	.004	.004	.003	.002	.001	.05
.10	.020	.019	.017	.015	.013	.011	.009	.007	.005	.003	.001	.10
.15	.030	.028	.025	.022	.019	.016	.013	.010	.008	.005	.002	.15
.20	.040	.037	.035	.029	.025	.021	.018	.014	.010	.006	.002	.20
.25	.050	.046	.041	.036	.031	.026	.022	.017	.012	.007	.002	.25
.30	.059	.054	.048	.043	.037	.032	.026	.020	.015	.009	.003	.30
.35	.068	.062	.056	.049	.043	.036	.030	.023	.017	.010	.004	.35
.40	.076	.069	.062	.055	.048	.041	.034	.026	.019	.012	.004	.40
.45	.083	.076	.068	.060	.053	.045	.037	.029	.021	.013	.004	.45
.50	.090	.082	.074	.065	.057	.049	.040	.032	.023	.014	.005	.50
.55	.096	.087	.078	.070	.061	.052	.043	.034	.024	.015	.005	.55
.60	.100	.091	.082	.073	.064	.055	.045	.035	.025	.016	.005	.60
.65	.103	.094	.085	.076	.066	.056	.047	.037	.026	.016	.005	.65
.70	.105	.096	.086	.076	.067	.057	.047	.037	.027	.016	.005	.70
.75	.103	.094	.085	.075	.066	.056	.046	.036	.026	.016	.005	.75
.80	.099	.090	.081	.072	.062	.053	.044	.034	.024	.015	.005	.80
.85	.090	.081	.073	.064	.056	.047	.039	.030	.022	.013	.004	.85
.90	.074	.067	.059	.052	.045	.038	.031	.024	.017	.010	.004	.90
.95	.047	.041	.037	.032	.028	.023	.019	.014	.010	.006	.002	.95
1.00	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	1.00

The values in table 3 were obtained by application of formulas 1 and 2. First, for various values of sx the corresponding values of R_0 and R_1 were computed from formula 2. Second, these values of R_0 were plotted against the ratio, R_0/R_1, which is ideal contrast ratio, C, and a smooth curve drawn through the points (see fig. 1, lower curve). Third, for enough values of C to determine the relation, $C_{R'}$ was computed by formula 1, the value of R_0 corresponding to each value of C being read from the curve (see fig 1); this was done for R' equal to 0.97, and for R' equal to 0.96, 0.94, 0.92, . . . 0.76. Fourth, the differences $C_{R'}-C_{.97}$ were computed, and the corrections given in table 3 obtained by graphical interpolation.

These corrections apply strictly to thin, homogeneous samples of material having a reflectivity (R_∞) of 0.80. In order to determine how accurately these corrections apply to actual samples, 13 papers were selected and R_0 and $C_{.96}$ measured for them. From these results values of ideal contrast ratio, C, were computed by formula 1. These values are plotted in fig 1 (circles). Figure 1 also shows the straight line, $R_0=C$, which refers to nonabsorbing samples ($R_\infty=1$). It is seen that the points representing actual paper samples fall about as much on one side of the curve for $R_\infty=0.80$ as on the other. For samples on or near the curve, the corrections of table 3 apply exactly; for those which fall far from it the corrections apply less exactly.

Table 4 shows values of R_0 and $C_{.96}$, obtained by measurement, and computed values of ideal contrast ratio, C, true contrast ratio, $C_{.97}$, and TAPPI opacity computed as $C_{.89}$. The differences, $C_{.89}-C_{.97}$, are also compared with the corrections read by interpolation from table 3. The final column gives the difference between $C_{.89}-C_{.97}$ and the corresponding correction read from table 3; it is seen that, as expected,

the corrections are appreciably in error both for papers of very light color (100 percent rag bond) and for dark papers (newsprint), but they apply well to papers of intermediate lightness.

It may also be noted that the corrections of table 3 apply well to the solid-opal-glass standards (see point indicated by square in fig. 1).

V. OPACITY ACCORDING TO THE TAPPI DEFINITION

The definition of opacity for paper adopted by the Technical Association of the Pulp and Paper Industry [17] was intended to be

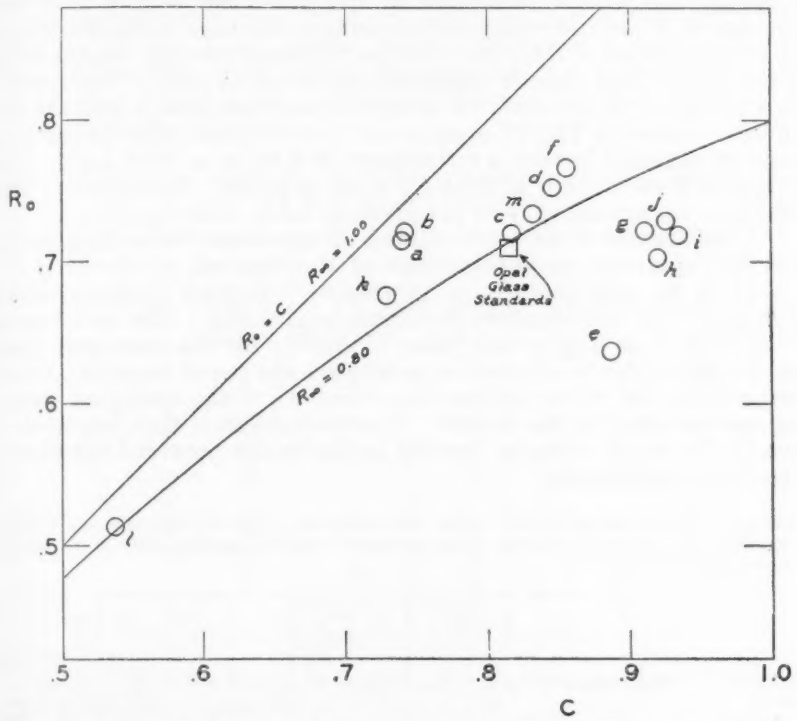

FIGURE 1.—*Relation between ideal contrast ratio, C and reflectance with black backing, R_0.*

The straight line, $R_0 = C$, refers to nonabsorbing samples ($R_\infty = 1.00$); the curve refers to samples made of various thicknesses of a material whose reflectivity (R_∞) is 0.80. The circles refer to paper samples identified in table 4.

equivalent to true contrast ratio, $C_{.97}$. However, the importance of the separation between sample and white backing was not well understood. As a result the method gives $C_{R'}$, where R' is somewhat lower than 0.97 because of interposition of a cover glass and is somewhat undefined because the reflectance of magnesium carbonate used as the white backing is not always the same and because the amount of separation is not stated. Much of the undesirable effect of this uncertainty in practice has been avoided by having many of the opacimeters compared with the instrument at the National Bureau of Standards.

[17] See footnote 2, p. 282.

Opacity by the TAPPI method, therefore, is determined by the adjustment of this particular instrument rather than by definition. Although this adjustment may not have been absolutely constant over a period of years, still there is some interest in determining the value of R' which characterizes the Bureau of Standards opacimeter because that value is probably the most reliable determinant of TAPPI opacity that can be obtained.

Accordingly two of the standards, A4 and B4, and three paper samples, j, k, l, of known reflectance, R_0, and ideal contrast ratio, C, were measured on the Bureau of Standards instrument. It was found by the method described in the preceding section that the reflectance, R', of the cavity commencing at the back of the standards is 0.92, while that of the cavity, deeper by about 0.6 mm, commencing at the back of the thinner paper samples is about 0.89. The corrections for $R'=0.89$ obtained by interpolation from table 3 indicate the difference between TAPPI opacity and true contrast ratio for samples made of material having a reflectance of 0.80 in a thick layer; the difference rises as high as 0.04 for some samples. Examples of this difference for actual samples are given in table 4 as $C_{.89}-C_{.97}$.

If a standard is to be used to check an opacimeter according to the TAPPI definition, an abridgement of the method of checking described in the previous section is possible. Instead of giving values of R_0 and C for the standard it suffices to give $C_{.92}$. The instrument is adjusted so as to give this value of opacity for the standard; then the sample holder is adjusted so as to place the paper samples 0.6 mm further from the white backing than the back of the opal-glass standard inserted without the holder. The instrument is then adjusted to give $C_{.89}$ for paper samples inserted in the holder provided the photometer is in adjustment.

TABLE 4.—*Ideal contrast ratio, C, true contrast ratio, $C_{.97}$, and approximate* TAPPI *opacity, $C_{.89}$, for representative paper samples showing applicability of the corrections given in table 3*

Sample	Type of paper	R_0	$C_{.94}$	C	$C_{.97}$	$C_{.89}$	$C_{.89}-C_{.97}$	Corrections read from table 3 for $R'=.89$	Error in the correction
a	100 percent rag bond	0.715	0.765	0.740	0.759	0.803	0.044	0.039	+0.005
b	do	.721	.768	.742	.761	.806	.045	.038	+.007
c	Book, no filler	.720	.837	.817	.832	.866	.034	.033	+.001
d	Book, clay filler	.753	.865	.846	.861	.892	.031	.028	+.003
e	Newsprint	.637	.897	.887	.895	.913	.018	.025	−.007
f	Book, clay filler	.767	.875	.856	.870	.901	.031	.028	+.003
g	do	.722	.922	.911	.919	.936	.017	.021	−.004
h	do	.703	.929	.920	.927	.942	.015	.018	−.003
i	do	.719	.943	.935	.941	.954	.013	.016	−.003
j	do	.729	.935	.926	.933	.948	.015	.017	−.002
k	Sulphite bond	.676	.752	.729	.747	.788	.041	.039	+.002
l	Manifold	.513	.558	.538	.553	.593	.040	.040	±.000
m	Mimeograph	.734	.851	.832	.847	.879	.032	.030	+.002

An abridged method of obtaining a calibration of the instrument for paper samples represented closely by the curve of figure 1 is also possible, provided the difference, $\Delta C_{.92}$, between the true value of

$C_{.92}$ for the standard and opacity given for it by the instrument is not too great (perhaps less than 0.03). This difference, $\Delta C_{.92}$, is a measure of how much the reflectance of the cavity departs from 0.92. To a first approximation the reflectance of the deeper cavity (deeper by 0.6 mm) commencing at the back of the paper sample will depart from 0.89 by the same amount, and the opacimeter will give a result correspondingly in error, say by $\Delta C_{.89}$. By application of formulas 1 and 2 as described in connection with table 3, the relation of $\Delta C_{.92}$ and $\Delta C_{.89}$ can be determined so that the corrections, $\Delta C_{.89}$, to be applied to readings on paper samples may be found directly from the correction for the standard, $\Delta C_{.92}$, without the need for computing R' explicitly. Table 5 gives the ratio, $\Delta C_{.89}/\Delta C_{.92}$, as a function of opacity, $C_{R'}$, given by the instrument assuming that the standard has $C_{.92}=0.85$, which is nearly true for the solid-opal-glass standards. These ratios may also be found from table 3 by taking the appropriate differences.[18]

TABLE 5.—*Relation between the corrections for paper samples, $\Delta C_{.89}$, and the correction for the standard, $\Delta C_{.92}$*

[These values are for papers having reflectivities ($R\infty$) of about 0.80]

Measured value of opacity $C_{R'}$	Ratio of error for a paper sample to error for the standard $\Delta C_{.89}/\Delta C_{.92}$	Measured value of opacity $C_{R'}$	Ratio of error for a paper sample to error for the standard $\Delta C_{.89}/\Delta C_{.92}$
0.00	0.0	0.50	1.0
.05	.1	.55	1.1
.10	.2	.60	1.2
.15	.3	.65	1.2
.20	.4	.70	1.2
.25	.5$_5$	.75	1.2
.30	.7	.80	1.1$_5$
.35	.7$_5$	.85	1.0
.40	.8$_5$	.90	.8
.45	.9	.95	.5
		1.00	0

The use of these ratios to find $C_{.89}$ for a paper sample is illustrated by the following example:

True value for $C_{.92}$ for the standard		0.854
Opacity of standard measured by instrument		.870
Instrument reads high by $\Delta C_{.92}$ equal to		.016
Opacity of a book paper by instrument, $C_{R'}$		.925
Ratio from table 5 for $C_{R'}=0.925$	0.7	
Correction, 0.016 x 0.7		.011
$C_{.89}$ for the book paper		.914

WASHINGTON, JULY 6, 1934.

[18] Detailed instructions for checking opacimeters of the type described in Bureau of Standards Circular C63 according to this method are given in NBS Letter Circular LC418, Standards for Checking Opacity Meters.

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INTERFERENCE MEASUREMENTS IN THE SPECTRA OF NOBLE GASES

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ABSTRACT

Employing the Fabry-Perot étalon interferometer, the wave lengths corresponding to lines in the first spectra of the noble gases have been measured relative to the fundamental standard of wave length (Cd 6438.4696 A), and to selected red lines of neon previously compared with the primary standard. The observations range from the violet (3948 A) to the infrared (10830 A). Values are given for 3 lines of He, 172 of Ne, 87 of A, 55 of Kr, and 130 of Xe. Many of the lines have been found to be reproducible to eight figures, and are regarded as highly satisfactory standards in spite of objections which have been raised against them on account of isotopic hyperfine structure.

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I. INTRODUCTION

The specification and adoption of international standards of wave lengths for spectroscopy and astrophysics has been one of the functions of the International Astronomical Union since 1922. A wave length of the red radiation from cadmium vapor, evaluated by comparison with the meter, was adopted as the primary standard,[1] and from time to time wave lengths from other sources interferometrically compared with the primary standard by three independent observers have been adopted as secondary standards in various parts of the spectrum. These secondary standards consist mainly of values from the spectrum of the iron arc [2] but include also 24 orange and red lines of neon,[3] and 10 blue lines of krypton.[4] Geissler tubes containing noble gases possess many desirable properties as sources of wavelength standards, and interference measurements in the spectra of these gases have been made at this Bureau since 1911.[5] One or more

[1] Trans. I.A.U. **2**, 232(1925).
[2] Trans. I.A.U. **3**, 86(1928).
[3] Trans. I.A.U. **2**, 41,232(1925).
[4] Trans. I.A.U. **4**, 76(1932).
[5] Bul.BS **6**,573(1911).

sets of values for the stronger lines of helium,[6] neon,[7] argon,[8] krypton,[8] and xenon [8] have already been published. During the past 2 years new types of photographic emulsions and sensitizers have become available, and following preliminary study of grating spectra,[9] an effort was made to extend the interference measurements in noble gas spectra to include both longer waves and fainter lines than had been observed heretofore. The results of these measurements are reported in this paper.

Before presenting our experimental procedure and results, we shall discuss briefly the status of the primary standard, and the general qualifications of noble gases as sources of standard wave lengths.

In order to correct some divergences found among the methods employed by spectroscopists, the I.A.U. Committee on Standards of Wave Length and Tables of Solar Spectra recommended [10] in 1925 "that the Union adopt provisionally the following specifications for the production of the primary standard of wave length: the primary standard of wave length, λ6438.4696 of cadmium, shall be produced by high voltage electric current in a vacuum tube having internal electrodes. The lamp shall be maintained at a temperature not higher than 320° C. and shall have a volume not less than 25 cubic centimeters. The effective value of the exciting current shall not exceed 0.05 amperes. At room temperature, the tube shall be nonluminous when connected to the usual high voltage circuit."

The Union actually adopted the following specifications: [11]

"L'étalon primaire de longuer d'ondes, λ6438.4696 du cadmium, sera prodiut par un courant électrique à haute tension dans un tube à vide portant des électrodes intérieures. La lampe sera maintenue à une température ne dépassant pas 320° C., et devra donner des différences de marche d'au moins 200,000 longuers d'ondes. La valeur efficace du courant d'excitation ne dépassera pas 0.05 ampere. À la température de la salle le tube ne sera pas lumineux quand il sera connecté au circuit habituel à haute tension."

In 1927 the International Conference on Weights and Measures also adopted the red radiation from cadmium vapor as the primary standard of wave length,[12] but the specifications of the source differ somewhat from those adopted by the I.A.U. "Dans l'état actuel de nos connaissances, il est recommandé que la Conférence adopte, comme étalon fondamental pour la longuer des ondes lumineuses, la longuer d'onde de la radiation rouge émise par la vapeur de cadmium, déterminée par les expériences de MM. Benoit, Fabry et Perot. D'aprés ces expériences, la longuer d'onde de cette radiation est $6438.4696 \times 10^{-10}$ mètre, lorsque la lumière se propage dans l'air sec à 15° (echelle de l'hydrogene), à la pression de 760 mm de mercure, g equivalent à 980,665 cm/sec^2, valeur normale de la pesanteur, La lumière doit être produite par un courant électrique de haute tension, continu, ou alternatif de fréquence industrielle (a l'exclusion de la haute fréquence), dans un tube a vide ayant des électrodes intérieures. La lamp doit avoir un volume ne dépassant pas 25 cm^3 et un tube capillaire dont le diamètre ne soit pas inférieur à 2 mm; elle doit être

[6] Bul. BS **14**,159(1917).
[7] Bul. BS **14**,765(1918).
[8] BS Sci. Pap. **17**,193(1921).
[9] BS J. Research **9**,121(1932); **10**,139(1933); **10**,427(1933).
[10] Trans. I.A.U. **2**,40(1925).
[11] Trans. I.A.U. **2**,232(1925).
[12] 7 Conf. Gen. des Poids et Mesures, 52(1927).

maintenue a une température voisine de 320°, et la valeur du courant qui la traverse ne doit pas excéder 0.02 ampère. A la température ambiante, le tube ne doit pas être lumineux lorsque le circuit à haute tension y est établi."

This specification is based upon the actual tube and operating conditions used for the comparison of the cadmium waves with the meter, and is, therefore, to be preferred.[13] The I.A.U. specification is less restricted, it does not exclude high-frequency excitation, it does not mention the volume or capillary bore of the tube, but requires that it must give interferences with differences of path of at least 200,000 waves. The condition that the interference limit may be 200,000 waves is objectionable since this is less than half of the theoretical or actual limit of the Michelson tube, and cadmium sources in which any such reduction in interference order occurs will certainly yield a different value for the primary standard. Up to the present time the Michelson tube has always been used for the most precise comparisons of wave lengths with meters, and of the secondary standards. The results have justified the retention of the red cadmium line emitted by the Michelson lamp as a reliable standard of length, and indicate that the cadium, neon and krypton scales are identical within 1 part in 50 millions.

It has been variously proposed to substitute the krypton lines 5562 A[14] and 5649 A[15] for the red cadmium line as a primary standard. These lines have relatively low intensity, they involve metastable states of the atom which favor self-reversal, and since krypton lines have been found to show complex hyperfine structure it is doubtful if any of them are suitable as primary standards.[16] The abovementioned lines of krypton have been examined for hyperfine structure by Romanova and Ferkhmin,[17] who report that Kr 5562 A shows four strong satellites (+0.0020, +0.0040, −0.0016, −0.0033A) and four weak ones (+0.0060, +0.0075, −0.0060, −0.0079A) while Kr 5649 A possess three strong satellites (+0.0014, +0.0034, −0.0020A) and three faint ones (+0.0068, +0.0092, −0.0080A). The same observers claim to have found hyperfine structure in Cd 6438 as emitted by a cooled Schüler tube; they report two strong satellites (−0.0034, +0.0035A) and one faint diffuse one (+0.0092A).

Under extraordinary operating conditions Perard [18] has found a narrow but symmetrical self-reversal in the red radiation from cadmium, and express the opinion that this possibility of reversal renders it unsuitable for use as a fundamental unit of length.

The observations of hyperfine structure and of self-reversal in the red line of cadmium are really beside the point because neither applies to the radiation emitted by the Michelson tube under the conditions specified by the International Conference of Weights and Measures. Under these conditions the line has always been found to be simple, sharp and symmetrical, and comparisons with the meter and with selected lines in the spectra of noble gases have demonstrated that it is reproducible to a very high degree.

[13] Trans. I.A.U. **4**, 233(1932).
[14] Compt. Rend. **194**,1633(1932).
[15] Phys. Z. **29**,233(1928).
[16] BS J.Research **3**,160(1929).
[17] Compt. Rend. Acad. Sci. USSR Nouvelle serie no. [2]57(1933). C.R. **198**,727(1934).

According to Aston [19] cadmium had 6 isotopes which in order of intensity have atomic weights 114, 112, 110, 113, 111, and 116. The hyperfine structure of triplet terms in the Cd I spectrum is ascribed by Schüler to a nuclear spin moment of ½ unit for the odd isotopes, and intensity measurements indicate that these constitute 23 percent of all isotopes.[20]

From a study of the polarization of resonance radiation, and Paschen-Back effect, Heydenberg [21] concludes that the separation of the odd isotope levels of $^1P_1$ (final state for 6438 A) is 0.0126 cm^{-1}, the stronger components from the even isotopes fall between these limits and determine the center of gravity, so the red line, even if complex, may be expected to be symmetrical. It may be added that the half width of the red line from cadmium, if the entire width be ascribed to Doppler-Fizeau effect, is 0.005 A, which is in close agreewith 0.006 A measured by Michelson.[22]

With regard to reversibility it is appropriate to look again at the atomic origin of the red line of cadmium.[23] This line represents the transition $5\ ^1P_1 - 5\ ^1D_2$, and the absolute values of the spectral terms are 28,846.60 and 13,319.24, respectively. The normal state of the cadmium atom is represented by $5\ ^1S_0 = 72{,}538.81$, which is 43,692.21 cm^{-1} (nearly 5 volts) lower in energy than $5\ ^1P_1$ so that only cadmium atoms which have been excited by 5-volt electrons are capable of absorbing the red radiation. Furthermore since $5\ ^1P_1$ is not a metastable state it is only under extraordinary conditions that the red line can be observed spontaneously reversed.

Consideration of the above facts leads us to the conclusion that the red radiation emitted by cadmium under the conditions laid down by the International Conference of Weights and Measures remains the most satisfactory fundamental standard of length, and we have accordingly used it again in the wave length measurements in spectra of the noble gases.

Geissler tubes containing noble gases are at present the most convenient and reproducible sources of secondary standards of wave length. When filled with pure gases at low pressure (5 to 15 mm Hg) they emit narrow lines of considerable intensity and if the capillary is viewed side-on it is quite unusual to observe any self-reversal in the lines. Their strongest lines (aside from those in the extreme ultraviolet) lie in the visible and infrared regions and it is especially in the long-wave range that they will be most useful as secondary standards since new types of emulsions and sensitizers have extended the photographic limit of spectroscopy. Aside from hyperfine structure (and Zeeman and Stark effects), the width of spectrum lines excited at low pressure is accounted for by the Doppler-Fizeau effect of the radiating particles, and according to kinetic theory the limiting order of interference (which is a measure of the sharpness of a line), $N = 1.22 \times 10^6 \sqrt{\frac{m}{T}}$ where m is the atomic mass and T the absolute temperature. Since Geissler tubes of the noble gases can be operated at low temperatures, the heavier gases in particular should give exceptionally sharp lines capable of producing interfer-

[19] Phil. Mag. **49**,1191(1925).
[20] Z. Phys. **67**,433(1931).
[21] Phys. Rev. **43**,640(1933).
[22] Travaux et Memoires **11**,143(1895); **15**,7,(1913).
[23] 7. Conf. Gen. des Poids et Mesures, 85(1927).

ence patterns over relatively large paths. This was tested experimentally by Buisson and Fabry [24] who observed the limiting orders of interference for He, Ne, and Kr lines excited at ordinary temperature and at the temperature of liquid air, as reported in table 1.

TABLE 1.—*Limiting orders of interference*

Gass	Atomic mass	Wave length	Ordinary temperature (290° K.)		Liquid air temperature	
			$N_{obs.}$	$N_{calc.}$	$N_{obs.}$	$N_{calc.}$
He	4	5,876	144,000	144,000	241,000	249,000
Ne	20	5,852	324,000	321,000	515,000	555,000
A	40			455,000		787,000
Kr	83	5,570	600,000	597,000	950,000	1,033,000
Xe	128			750,000		1,300,000

Reversibility is an important consideration among the credentials of spectral lines as wave length standards. In any spectrum the lines most readily absorbed or reversed are those which involve the final or normal state of the atom. Since the neutral atoms of noble gases in every case have completely filled electron shells (s^2 for He and $s^2\ p^6$ for Ne, A, Kr, Xe, Rn) their normal unexcited states are represented by a $^1S_0$ spectral term. Because of the high stability of these configurations this term corresponds to a relatively large energy and combinations with it are found only in the extreme ultraviolet. The more familiar spectra of the noble gases arise from terms associated with higher quantum states, for example in Ne I the well-known group of yellow, orange, and red lines represent transitions $(s^2\ p^5)\ s - (s^2\ p^5)\ p$ in which the first configuration represents $^1P_1$ and $^3P_{0,\ 1,\ 2}$ (levels s_2, s_3, s_4, s_5, in Paschen's notation),[25] while the second configuration represents a group of more highly excited states. The final states in this case are about 135,000 cm^{-1} above the normal state so that none of these lines would be expected to show spontaneous self-reversal. However, two of the final states, $^3P_0$ and $^3P_2$, on account of the selection rule for inner quantum numbers, cannot combine with the normal state $^1S_0$, and are therefore metastable. Relatively long life of atoms in such metastable states favors absorption by these levels so that neon lines (or any corresponding lines in other noble gases) which are connected with levels s_3 or s_5 in Paschen's notation can exhibit partial reversal,[26] as Meissner proved. The lines connected with the s_2 and s_4 levels on the other hand are relatively free from such effects.

Unfortunately, excepting helium (and perhaps radon, for which no information is available), the spectral lines of the noble gases are afflicted with hyperfine structure of two or more components which impairs any claim which might be made for them as ideal monochromatic standards. This hyperfine structure arises from the isotopic constitution of the noble gases, it can only be eliminated by separation of the isotopes and utilization of a single even-numbered atomic mass. Two types of isotopic fine structure of spectral lines occur, one type

[24] J. de Phys. 2,442(1912).
[25] Ann. Phys. [4]60,405(1919).
[26] Ann. Phys. 76,124(1925).

(isotopic displacement) is displayed by components of even numbered atomic masses (without moments of nuclear spin) and the other (nuclear spin structure) is generally revealed as a coarser pattern of several components associated with each odd-numbered isotope (having moment of nuclear spin).

For the nobles gases the mass numbers in order of the intensities of the mass-spectrum lines are, according to Aston,[27] as given in table 2.

TABLE 2.—*Isotopes of noble gases*

Element	Atomic number	Atomic weight	Mass numbers
He	2	4.00	4.
Ne	10	20.2	20, 22.
A	18	39.91	40, 36.
Kr	36	82.9	84, 86, 82, 83, 80, 78.
Xe	54	130.2	129, 132, 131, 134, 136, 128, 130, 126, 124.

Thus, He spectral lines will be free from isotopic fine structure, Ne and A lines may show one satellite due to the less abundant isotope, Kr lines may consist of a group of components due to even isotopes and an additional pattern arising from the odd isotope, while Xe lines may be expected to be exceedingly complex on account of almost equal abundance of odd and even isotopes, the spin moments of the former and the large number of the latter.

The difficulties which hyperfine structures add to wave length comparisons are, however, much less serious than here implied since mitigating factors are found in the abundance ratios of the isotopes. Thus in Ne the second isotope is only 10 percent of the whole, while in A it is of the order of 1 percent. When observations are made photographically these faint satellites are never detected except with overexposure of the main components and very high resolving power. This explains why the Ne satellites were not discovered until 1927, and also why the A satellites remain hidden at the present time. That such faint satellites can have no appreciable effect on wave-length comparisons is shown by the almost perfect agreement of the values for Ne lines determined at this Bureau [28] before the discovery of Ne isotopes or satellites, with the recent measurements of Jackson.[29] In the former case there was no consciousness of a disturbing factor while in the latter only high resolving powers were found to yield constant values, yet the mean accidental difference between the two sets of values is ± 0.0002 A and the systematic difference is well under 0.0001 A. Similar agreement is found between values of violet krypton lines compared with Ne standards by Humphreys [30] and with Cd 6438 A by Jackson.[31] These matters will be discussed in greater detail in connection with the results presented below.

II. EXPERIMENTAL

The theory of wave-length comparisons with the Fabry-Perot interferometer was first given by Fabry and Buisson,[32] it has become so

[27] I.C.T. 1,45(1926).
[28] Bul.BS 14'765(1917).
[29] Proc. Roy. Soc. [A]143,124(1933).
[30] BS J. Research 5,1041(1930).
[31] Proc. Roy. Soc. [A]138,147(1932).
[32] Astrophys. J. 28,169(1908).

familiar that it is unnecessary to repeat it—reference may be made to a paper by Humphreys,[33] which contains an outline of the methods used also in the reduction of the present observations.

The primary standard was the red radiation from cadmium, emitted from a Michelson tube in accordance with the conditions specified by the International Conference of Weights and Measures. Spectra of the noble gases were obtained from Geissler tubes purchased from Robert Goetze in Leipzig. These tubes were provided with narrow capillaries (about 1 mm bore) to concentrate the luminous discharge and were always used side-on. Cadmium and noble gas tubes were connected in series to the secondary of a transformer which forced a current of 10 to 20 ma through the lamps. For a considerable number of exposures, especially those of longest duration, the neon lamp was used as a source of standards, since the mean of a group of red neon lines is regarded as equivalent to the primary standard.[34] Since the values of neon lines adopted by the I.A.U. are given only to 3 decimals the mean of 4-decimal values determined at this Bureau [35] and by Jackson [36] were adopted for purposes of these recent comparisons.

In order to obviate possible difficulties due to small changes in temperature or barometric pressure which may occur during exposures, alternate exposures of primary and secondary sources were avoided. Both sources were adjusted so as to illuminate the interferometer and spectograph in like manner, and then exposed simultaneously.

The interferometer consisted of silvered quartz plates of 6 cm aperture separated by invar étalons of 3, 6.2, 10, 15, 25, 35, or 43 mm length. The first 2 étalons were employed only for preliminary refinements of wave-length values and for determining the dispersion of phase at reflection by comparison with values obtained from the 43-mm separator.[37]

Two different series of observations were made with the same plates, but the silver films were renewed for the second series. Comparisons with the primary standard constitute part of the second series. Dispersion of phase change at reflection was determined for each silvering and in the second case both before and after the observations since an interval of more than a year had elapsed during which the silver had tarnished considerably. The second determination of phase dispersion checked the first for the longer waves but gave a larger correction in the region of short waves. These corrections must be determined with care if values to 4 decimals are desired for lines which occur several thousand angstroms removed from the primary standard, since even with the highest orders of interference they may amount to as much as a unit in the third decimal place. This is perhaps the most important step in precise measurements of wave lengths by the Fabry-Perot interferometer method. Interference patterns were projected on the slit of the spectrograph by means of achromatic lenses having 25 cm or 50 cm focal length, the short focus lens being used only in connection with the two shortest étalons.

Both a Hilger E_2 spectrograph with glass prism, and a 21-foot concave grating mounted so as to give stigmatic images,[38] were employed

[33] BS J. Research **5**,1041(1930).
[34] Trans. I.A.U. **2**,41(1925).
[35] Bul. BS **14**,765(1917); J. Opt. Soc. Am. **11**,301(1925).
[36] Proc. Roy. Soc. [A] **143**,124(1933).
[37] Bul.BS **12**,199(1915).
[38] BS Sci.Pap. **18**,191(1922).

as dispersing and recording instruments. The grating was especially useful in the infrared where it separated the patterns of close lines not resolved on the prism spectrograms.

Several different types of photographic plates were tried in making the spectrograms, but all were prepared by the Research Laboratory of the Eastman Kodak Co.[39] In succession, emulsion types I, III, and finally a new type designated by 144, were employed, the last giving the greatest satisfaction on account of increased contrast and greatly reduced graininess. These emulsions were sensitized with one or more of the following Eastman types of sensitizers, F, R, P or Q. Plates sensitized only to the infrared lacked sufficient red sensitiveness to record the primary standard, but this was remedied by adding a little pinacyanol solution to the hypersensitizing bath of dilute ammonia with which all dyed plates are treated just before use.

III. RESULTS

New determinations of wave lengths in the first spectra of the noble gases are presented in 5 tables which follow in atomic order, He, Ne, A, Kr, and Xe. In these tables the whole number in angstrom units appears in the first column and the fractional part in succeeding columns. Values derived from the primary standard (Cd 6438.4696 A) and from the red lines of neon are listed separately, and some of the best data from other sources are added for purposes of comparison. Only the 25 and 35 mm étalons were used in the first, and the values relative to neon are based principally on measurements of spectrograms with the 43 mm étalon. All values are corrected to standard atmospheric conditions by consulting the tables published for this purpose by Meggers and Peters.[40] Unfortunately, since nothing is known about the dispersion of water vapor, it is impossible to calculate the appropriate corrections for humidity, but we can probaby assume that this second-order effect is negligible.

In the tables below only the values for the principal component of complex lines is given, all data on hyperfine structure being omitted. The number of observations is reported with each wave-length value to serve as a rough index of the reliability. Only when the individual determinations with high orders indicate that the probable error of the mean is less than 0.001 A is the fourth decimal retained. The symbol hf means that hyperfine structure has been detected for the line it accompanies.

1. HELIUM

Values for 21 of the most intense He I lines (2945.104 to 7281.349) were determined relative to the primary standard by Merrill.[41] In the infrared, the group at 10830 A was recorded with phosphorophotography by Ignatieff [42] in 1914; it is now within range of ordinary photography and has been measured relative to neon standards. On account of the low atomic mass of He, the lines from uncooled tubes are intrinsically wide and incapable of producing interference patterns with large retardations. With the fixed étalons which were available, the best resolution of the infrared He lines was obtained with separations of 6.2 and 15 mm. The spectrograms were made with the con-

[39] J. Opt. Soc. Am. **21**,753(1931); **22**,204(1932); and Addendum (February 1932).
[40] Bul.BS **14**,724(1918).
[41] Bul.BS **14**,159(1917).
[42] Ann. Phys. [4],**43**,1117(1914).

cave grating, the infrared He lines being recorded in the first-order spectrum on 144–Q plates, and the red Ne standards in the second-order spectrum on III–F plates. Corrections for dispersion of phase between 6400 and 10830 A were avoided in this case by dividing the difference in interference path, 2 (15–6.2), for the first point by the corresponding difference in orders for the second. The results are shown in table 3.

TABLE 3.—He I *interference measurements*

λ air	ν vac	λ Ignatieff
10829.081	9231.866	10829.11±0.02
10830.250	9230.870	10830.32± .01
10830.341	9230.792	

This group represents the transition $^3S_1 - ^3P^0_{0,1,2}$ in which the threefold P term is responsible for 3 lines. The second interval of this term is abnormally small and was not resolved until 1927 when both Hansen [43] and Houston [44] with interferometers of high resolving power and He tubes cooled with liquid air, succeeded in splitting the stronger components of certain visible He lines involving the same $^3P_{1,2}$ levels. The former reported the separations of the ^3P levels as 0.991 and 0.077 cm^{-1}, while our measurements of the infrared group yield 0.996 and 0.078 cm^{-1}. Without doubt these values could be still further improved by observing the infrared lines emitted by a cooled source permitting the use of larger orders of interference.

2. NEON

Beginning with neon, the first spectra of the noble gases become more complex, and in general, are shifted toward longer waves but exhibit the same features in gross structure. An extensive series of Ne wave-length measurements relative to the primary standard was made at this Bureau in 1918.[45] Similar determinations to 4 decimals for 20 yellow, orange and red lines were made in 1933 by Jackson [46] who justifies their use as secondary standards; both sets are quoted in table 4 where they may be compared with our new values. We have succeeded in extending the measurements to longer waves and to fainter lines.

The term structure of the Ne I spectrum was analyzed by Paschen [47] in 1919, and recently extended to include new lines observed in the infrared by Gremmer,[48] and by Meggers and Humphreys.[49]

In 1920 Aston [50] reported ordinary neon to consist of 2 isotopes with mass numbers 20 and 22 in the ratio of 9 to 1, and in 1927 Hansen [51] detected that the strong neon lines (from mass 20) were accompanied on the short wave side by faint satellites (from mass 22). This isotope displacement amounts to −0.02 or −0.03A and

[43] Nature **119**,237(1927); Verh. D. Phys. Ges. **3**,5(1929).
[44] Proc.Nat.Acad.Sci. **13**, 91(1927).
[45] Bul.B.S. **14**,765(1918).
[46] Proc.Roy.Soc. [A] **143**, 124(1933).
[47] Ann. Phys. [4] **60**, 405(1919).
[48] Z. Phys. **50**,716(1928).
[49] BS.J.Research 10, 429(1933).
[50] Nature **104**,334(1927).
[51] Nature **119**,237(1927).

has been studied in detail by Nagaoka and Mishima [52] and by Thomas and Evans.[53] These faint satellites are difficult to detect, and it is apparent from a comparison of the various determinations of wavelength values that they have no appreciable effect on reproducibility or precision of measurement. The uncertainty in value of well determined Ne lines is obviously less than 0.001 A and retention of the fourth decimal place seems justified in such cases.

Perard [54] has reported that certain Ne lines exhibit variable wave length, especially when the orders of interference exceed about 100,000 but we have been unable to confirm such variations. The only line for which we have detected any abnormal behavior is 6402 which appears to be unsymmetrically reversed with étalons of 35 or 43mm length. This line represents the strongest combination with the s_5 level which has the longest metastable life; in Meissner's experiment it was 74 percent absorbed.

TABLE 4.—Ne I *interference measurements*

Structure	λA	Cd standard	Obs.	Ne standards	Obs.	NBS [1] Cd standard	Jackson [2] Cd standard	Structure	λA	Cd standard	Obs.	Ne standard	Obs.	NBS [1] Cd standard	Jackson [2] Cd standard
	4334			125	2				4614			391	4		
	4363			524	3				4617			837	3		
	4381			220	2				4628			309	5		
	4395			556	3				4636			125	4		
	4422			519	5				4636			634	4		
	4424			800	5				4645			416	5		
	4425			400	2				4649			904	3		
	4433			721	3				4656			3923	6		
	4460			175	4				4661			104	5		
	4466			807	4				4670			884	3		
	4475			656	3				4678			218	4		
	4483			190	4				4679			135	4		
	4488			0928	6				4687			671	4		
	4500			182	2				4704			395	5		
	4517			736	3				4708			854	2		
	4525			764	3				4715			344	5		
	4537			751	4				4725			145	4		
	4540			376	4				4749			572	4		
	4552			598	2				4752			7313	6		
	4565			888	4				4758			728	2		
	4573			759	3				4780			338	3		
	4575			060	4				4788			9258	6		
	4582			035	4				4790			218	2		
	4582			450	4				4800			111	3		
	4609			910	4				4810			0625	6		

[1] BS Bull. **14**,769(1918).
[2] Proc. Roy. Soc. **A143**,131(1933).

[52] Proc. Imp. Acad. **5**,200(1929).
[53] Phil. Mag. **10**, 128(1930).
[54] Compt. Rendi **176**,375(1923); **184**,446(1927).

TABLE 4.—Ne I *interference measurements*—Continued

Structure	λA	Cd standard	Obs.	Ne standards	Obs.	Cd NBS standard	Cd Jackson standard	Structure	λA	Cd standard	Obs.	Ne standard	Obs.	Cd NBS standard	Cd Jackson standard
	4817			636	6				5433			649	2		
	4821			924	5				5448			508	2		
	4827			338	6				5562			769	5		
	4827			587	2				5656			6585	6		
	4837			3118	6				5662			547	2		
	4852			655	5				5689	817	1	8164	6		
	4863			074	5				5719	224	1	2254	6		
	4865			505	4				5748	298	1	299	6		
	4866			476	2				5764	4182	3	418	6	419	
	4884			915	5				5804	450	1	4488	6		
	4892			090	4				5820	1553	3	1548	7	155	
	4928			235	3			hf	5852	4878	8			4880	4876
	4939			041	4				5872			828	3		
	4944			987	4			hf	5881	8950	8			8954	8948
	4957			0334	6				5902	4634	2	464	4		
	4957			122	3				5906			429	3		
	4994			930	2				5913			633	4		
	5005			160	5			hf	5944	8340	8			8343	8343
	5011			003	2				5965			474	2		
	5022			870	2				5974			628	4		
	5031			3484	6			hf	5975	5343	8			5339	5340
	5037			7505	7				5987			9069	5		
	5074			200	6			hf	6029	9968	8			9970	9973
	5080			383	6			hf	6074	3376	8			3377	3377
	5104			705	2			hf	6096	1630	8			1630	1630
	5113			675	5				6128	4502	2	4513	6		
	5116	501	1	503	6			hf	6143	0627	7			0624	0620
	5122			257	4			hf	6163	5937	8			5937	5941
	5144			9376	7				6182			146	3		
	5151			963	6			hf	6217	2812	8			2811	2814
	5154			422	3			hf	6266	4952	8			4950	4949
	5156			664	2			hf	6304	7893	8			7890	7893
	5188			612	7			hf	6334	4276	8			4280	4280
	5193			130	3			hf	6382	9914	7			9913	9915
	5193			224	3			hf	6402	248	4	247	4	2455	2461
	5203			8950	7			hf	6506	5277	7			5278	5280
	5208			863	3			hf	6532	8824	8			8826	8824
	5210			573	3			hf	6598	9528	8			9528	9530
	5222			351	5			hf	6678	2766	8			2760	2766
	5234			028	3			hf	6717	0430	8			0427	0427
	5298			190	5			hf	6929	4679	6			4678	
	5304			756	2				7024			0508	6		
	5326			396	2			hf	7032	4125	5	4134	12	4130	
	5330	778	2	7766	7	779			7059	108	1	109	3		
	5341	093	2	091	6	096			7173	9390	5	9389	10		
	5343			284	5				7245	1668	6	1668	13		
	5355			422	2				7438	8988	6	8990	11		
	5360			012	2				7488	8717	5	8722	9		
	5374			975	2				7535	774	5	7750	8		
	5400	5620	3	5619	2	5620			7544			046	4		

TABLE 4.—Ne I *interference measurements*—Continued

Structure	λA	Cd standard	Obs.	Ne standards	Obs.	NBS Cd standard	Jackson Cd standard	Structure	λA	Cd standard	Obs.	Ne standard	Obs.	NBS Cd standard	Jackson Cd standard
	7943	1802	4	1802	6				8591	2585	5	2584	9		
	8082	4585	2	4580	6				8634	649	4	6480	10		
	8118	549	1	5495	5				8654	383	3	3835	10		
	8136	4058	5	4060	9				8679			491	2		
	8259			380	2				8681			920	4		
	8266	077	2	076	5				8780	6220	5	6223	7		
	8300	3257	5	3258	11				8783	755	5	755	7		
	8377	6070	6	6068	13				8853	864	2	867	5		
	8418	4275	5	4274	9				8865			759	4		
	8495	3604	6	3600	11				9486			680	1		
									9535			167	1		
									9665			424	3		

3. ARGON

An extensive description and analysis of the A I spectrum was published by Meissner [55] in 1916, and recently extended by Rasmussen [56] and by Meggers and Humphreys.[57] The first comparison of A wave lengths with the primary standard were also made by Meissner,[58] and Meggers [59] followed with similar ones. We are now presenting in table 3, new measurements, having observed additional lines and reduced the probable error for many lines to the point where the eighth figure (fourth decimal place) can be given.

Like neon, argon also consists of two (possibly three) isotopes. The mass numbers are 40 and 36 in the ratio of about 160 to 1. Up to the present time no satellites have been reported for A lines and we have not observed them even with overexposures of infrared lines for which the resolving power of a silvered interferometer is very high. On account of the very low intensity of this satellite (due to A^{36}) it is safe to assume that it cannot influence the value of the wave length measured for the strong component (due to A^{40}) under ordinary circumstances. With the same resolving power and type of source, the A I lines appear considerably sharper than Ne I lines, but this is mostly, if not entirely, a consequence of larger atomic mass. However, on account of the relatively high sharpness of argon lines, absence of hyperfine structure due to nuclear spin, and almost ideal freedom from isotopic displacements, it seems probable that among all of the noble gas spectra A I lines will be found best qualified to serve as wave-length standards or standards of length.

[55] Z. Phys. **37**,238 (1926); **39**,172 (1926); **40**,839 (1927).
[56] Z. Phys **75**,695 (1932).
[57] BS J.Research 10,437 (1933).
[58] Ann. Phys. [4] **51**,95 (1916).
[59] BS Sci.Pap.**1**,198 (1921).

TABLE 5.—*Argon* I *interference measurements*

Structure	λA	Cd standard	Obs.	Ne standard	Obs.	Meggers [1] Cd standard	Meissner [2] Cd standard	Structure	λA	Cd standard	Obs.	Ne standard	Obs.	Meggers [1] Cd standard	Meissner [2] Cd standard
	3948			977	4	980			5888			592	(2)		
	4044			4173	6	419			5912			084	3		
	4054			5250	3				5928			805	(2)		
	4158	5895	5	5896	4	591			6032			124	(2)	127	
	4164	1789	3	1788	3	180			6043			230	(2)		
	4181	8825	3	8826	3	884			6052			721	(2)		
	4190	7098	3			714			6059			373	(2)		
	4191	0270	2			027			6105			645	(2)		
	4198	3160	6	316	2	316			6170			183	(2)		
	4200	6738	6	674	2	676			6173			106	(2)		
	4251			1842	3	184			6416			315	(2)	307	
	4259	3607	5	3603	3	362			6752			832	3	831	
	4266	2855	5	2853	4	286			6965	4304	5	4302	10	429	432
	4272	1678	5	1680	4	169			7030			262	1	250	
	4300	1000	5	0995	7	101			7067	2177	5	2170	12	217	218
	4333	5601	4	5595	3	561			7147	0412	5	0406	7	042	
	4335	3363	3	3370	3				7272	9356	5	9357	9	935	
	4345			1666	4	168			7372			117	1	119	
	4363			7936	4				7383	9800	6	9800	13	979	978
	4423			9936	3				7503	8667	4	8676	12	867	868
	4510	7324	5	7322	10	733			7514	653	4	6510	12	651	648
	4522			3216	8	325			7635	1055	6	1053	13	106	107
	4589			2884	6				7723	761	2	7597	11	758	760
	4596			0964	8	096			7724	206	2	2064	11	210	210
	4628			4398	8	445			7891			075	1		
	4702			3151	8	317			7948	1756	6	1754	13	175	177
	4752			9381	4				8006	155	2	1556	12	156	158
	4768			6716	5				8014	785	2	7856	12	784	786
	4876			2596	5				8053			307	1		
	4887			9465	5				8103	6922	3	6922	12	693	691
	5162			2845	5				8115	3095	3	3115	12	307	310
	5187			7458	5				8264	5210	6	5209	13	522	525
	5221			270	2				8408	207	2	208	12	210	216
	5252			786	2				8424	646	2	647	12	646	650
	5421			346	2				8521	4406	6	4407	13	442	
	5451			650	2				8667	9435	6	9430	13		
	5495			8720	3				9122	9664	6	9660	12		
	5506			112	(2)[3]				9224	498	5	498	10		
	5558			702	3				9354			218	8		
	5572			548	(2)				9657			7841	10		
	5606			732	3				9784			5010	10		
	5650			7034	3				10470			051	4		
	5739			517	(2)										
	5834			263	(2)										
	5860			315	(2)										

[1] BS Sci.Pap. **17**,198(1921).
[2] Ann.Phys. [4]**51**,95(1916).
[3] Observed only with 3 mm étalons.

4. KRYPTON

General descriptions and analyses of the first spectrum of Kr have been published by Gremmer,[60] and by Meggers, deBruin, and Humphreys,[61] to which new data for infrared lines were later added.[62] The first interference measurements of krypton wave lengths were by Buisson and Fabry [63] who obtained 5570.2908 and 5870.9172 A for the bright green and yellow lines. Perard [64] measured 5570.2892 and 5870.9154 A. Wave lengths of a considerable number of the stronger lines have been measured with interferometers by Meggers,[65] Humphreys,[66] and Jackson.[67] These values will be found in table 6, together with new data.

Although krypton atoms have a relatively large mass and correspondingly narrow spectral lines, this advantage is offset by the fact that it has at least 6 isotopes including one of odd mass (84, 86, 82, 83, 80, 78 in order of intensity).[68] Sixteen of the stronger Kr lines (4273 to 5870 A) were examined with Lummer-Gehrcke interferometers by Gehrcke and Janicki;[69] they reported that all lines are sharp, especially 5,570 and 5,870 A. According to Perard [70] who studied the latter lines with a Michelson interferometer, each has two close satellites. The hyperfine structure of Kr lines has been studied recently by Humphreys [71] and by Kopferman and Wieth-Knudsen.[72] No isotopic displacements have been detected, but it appears that the components of the even isotopes coincide with the center of gravity of Kr^{83}, and analysis of observed hyperfine structures indicates that a mechanical moment of spin equal to or exceeding 7/2 units must be ascribed to the nucleus of the odd isotope. Fortunately this isotope constitutes only about 12 percent of the whole so that the resolvable satellites contain only a few percent of the total energy in krypton lines.

TABLE 6.—*Krypton* I *interference measurements*

Structure	λA	Cd standard	Obs.	Ne standard	Obs.	Meggers [1] Cd standard	Humphreys [3] Ne standard	Jackson [2] Cd standard	Structure	λA	Cd. standard	Obs.	Ne standard	Obs.	Meggers [1] Cd standard	Humphreys [3] Ne standard	Jackson [2] Cd standard
	4273	9698	4	9700	6	9696	9705	9702		4410						369	
	4282			9680	4	967	9698	9689		4418						769	
	4286			487	1		4875			4425			190	1		1909	
	4300			487	1		4877			4453	9178	3	9176	6	9174	9183	9179
	4318	5522	2	5526	3	552	5523	5522		4463	6902	3	6901	5	690	6897	6906
	4319	5800	4	5796	8	580	5798	5801		4502	3550	3	3544	5	354	3546	3548
	4351			3602	2		3605			4550						298	
	4362	6424	3	6418	6	6422	6429	6425		4812						607	
	4376	1218	3	1220	8	122	1217	1221	hf	5562	2255	3	2254	4	224	2251	2266
	4399			9667	2	969	9675	9673	hf	5570	2892	4	2893	6	2872	2890	2899

[1] BS Sci.Pap. **17**,201 (1921). [2] BS J.Research **51**,047 (1930). [3] Proc Roy. Soc. **A138**,151 (1932).

[60] Z. Phys. **73**,620 (1932).
[61] BS J.Research **7**,643 (1931).
[62] Z. Phys. **73**,779 (1932); BS J.Research **10**,443 (1933)
[63] Compt. Rend. **156**,945 (1913).
[64] Compt. Rend. **176**,1,060 (1923).
[65] BS. Sci.Pap.**17**,193 (1921).
[66] BS J.Research **5**,1,047 (1930).
[67] Proc. Roy. Soc. [A] **138**,147 (1932).
[68] Proc. Roy. Soc. [A] **126**,521 (1930).
[69] Ann. Phys. [4] **81**,314 (1926).
[70] Compt. Rend. **184**,447 (1927).
[71] BS J.Research **7**,453 (1931).
[72] Z. Phys. **85**,353 (1933).

TABLE 6.—*Krypton* I, *interference measurements*—Continued

Structure	λA	Cd standard	Obs.	Ne standard	Obs.	Meggers Cd standard	Humphreys Ne standard	Jackson Cd standard	Structure	λA	Cd. standard	Obs.	Ne standard	Obs.	Meggers Cd standard	Humphreys Ne standard	Jackson Cd standard
	5580			390	1					7746			828	1		831	
hf	5649			5625	2		5627			7854	8217	5	8212	3		823	
	5672			452	1					7913	4246	2	4238	2		443	
	5832			857	1					7928	5998	2	5994	2		602	
	5866			752	1					7982			406	1			
hf	5870	9154	4	9153	3	9137	9153	9167	hf	8059	5038	5	5039	4		5053	
	5993			8506	2				hf	8104	364	1	3642	3		3660	
	6012			158	1				hf	8112	902	1	898	2		9023	
	6056			128	1					8190	0542	5	0544	4		0570	
	6421			0283	2		028			8195			070	1			
	6456			2894	2	290	293			8263	2398	2	2398	3		2412	
	6652			239	1					8272			355	2			
	6699			228	1				hf	8281	049	1	0495	2			
	7224			103	1					8298	1077	2	1077	3		1091	
	7287						262			8412			428	1			
	7486			862	1		850		hf	8508	8701	5	8699	4		8736	
	7587	4132	5	4128	3	414	4135			8764			112	1			
	7601	5444	5	5442	4	544	5465		hf	8776	7490	5	7490	4		7498	
hf	7685	2460	4	2460	2		2472		hf	8928	6922	5	6918	4		6934	
hf	7694	5395	4	5391	3		5401			9751			759	4			

5. XENON

General descriptions and analyses of the first spectrum of xenon were published by Gremmer,[73] and by Humphreys and Meggers.[74] A few of the stronger lines were compared with the primary standard by Meggers [75] in 1917 and a larger number were measured relative to neon standards by Humphreys [76] in 1930. Additional measurements of the latter type were included in the complete description referred to [77] and are reproduced in table 7 after being averaged in some cases with still later observations.

Gehrcke and Janicki [78] were the first to find structure among Xe lines; they examined 42 lines (4,078 to 6,768 A) with Lummer-Gehrcke plates and found 4,501 and 4,734 A to be complex. More recently, hyperfine structure of xenon lines has been studied by Humphreys,[79] by Kopferman and Rindal,[80] and in considerable detail by Jones.[81] In general, Xe line patterns consist of a strong central component together with a number of fainter lines, the total intensity of which is nearly equal to that of the intense central component. The latter represents mainly the unresolved components due to even isotopes with mass numbers 124, 126, 128, 130, 132, 134, 136, which constitute 52.2 percent of the whole. The remaining

[73] Z. Phys. **59**, 154 (1930).
[74] BS J.Research **3**, 731(1929); **10**, 139(1933).
[75] BS Sci.Pap.**17**,193(1921).
[76] BS J.Research **5**,1,048(1930).
[77] BS J.Research **10**,139(1933).
[78] Ann. Phys. [4] **81**,314(1926).
[79] BS J.Research **7**,460(1931).
[80] Z. Phys. **87**,460(1933).
[81] Proc. Roy. Soc. [A] **144**, 587(1934).

components result from the action of moments of spin in nuclei of the odd isotopes, 129 and 131, which respectively account for 27.1 and 20.7 percent of the whole. The observed hyperfine structure indicates that the spin moment $I=0$ for all even isotopes, but $I=\frac{1}{2}$ for Xe^{129} and $I=3/2$ for Xe^{131}.

In view of the relatively large abundance of odd isotopes and intensity of hyperfine structure components the Xe I lines appear to be least suited among noble gas spectra as standards. However, if measurements are restricted to the main component, the reproducibility as shown in table 7 is of the same order as for the best lines in other spectra.

TABLE 7.—*Xenon I interference measurements*

Structure	λA	Cd standard	Obs.	Ne standard	Obs.	Meggers [1] Cd standard	Humphreys [2] Ne standard	Structure	λA	Cd standard	Obs.	Ne standard	Obs.	Meggers [1] Cd standard	Humphreys [2] Ne standard
	3948			163	2				5394			738	2		
	3950			924	6		925		5439			923	2		
	3967			5411	6		541		5460			037	1		
	3974			417	5				5488			555	1		
	3985			202	4				5552			385	4		
	4078			8202	7		8207		5566			615	4		
	4109			7089	7		7093		5581			784	4		
	4116			1147	7		1151		5618			878	3		
	4135			133	4		123		5688			373	2		
	4193			528	3		5296		5695			750	2		
hf	4203			695	5		6945		5696			477	2		
	4205			404	2				5715			716	2		
	4372			287	3				5716			252	3		
	4383			908	5		9092		5807			311	1		
	4385			768	6		7693		5814			505	3		
hf	4500			978	4	978	9772		5823			890	7		
hf	4524			6805	11	680	6805		5824			800	5		
hf	4582			7472	8	746	7474		5856			509	3		
	4611			8882	7		8896		5875			018	9		
hf	4624	2756	3	2754	4	275	2757		5894			988	9		
hf	4671	2258	3	225	4	225	226		5904			462	2		
	4690			970	4		9711		5922			550	2		
hf	4697			0208	7	020	020		5931			241	8		
hf	4734			1518	4	154	1524		5934			172	8		
hf	4792			619	7		6192		5974			152	2		
hf	4807			0190	7	019	019		5998			115	3		
	4829			708	3	705	709		6007			909	3		
	4843			2934	6		294		6111			761	6		
hf	4916			507	2		508		6111			951	6		
	4923			152	5		1522		6152			070	3		
	5028			2794	8		2785		6163			661	8		
	5162			711	2				6163			935	4		
	5362			244	1				6178			303	5		
	5364			626	1				6179			665	5		
	5392			795	3				6182			420	8		

[1] BS Sci.Pap.17, 202(1921).
[2] BS J.Research,5, 1,048(1930).

TABLE 7.—*Xenon* I *interference measurements*—Continued

Structure	λA	Cd standard	Obs.	Ne standard	Obs.	Meggers Cd standard	Humphreys Ne standard	Structure	λA	Cd standard	Obs.	Ne standard	Obs.	Meggers Cd standard	Humphreys Ne standard
	6198			260	7				6976			182	2		
	6200			892	2				7119			598	2		598
	6206			297	1				7283			961	1		
	6224			168	2				7285			301	2		298
	6261			212	6				7316			272	2		
	6265			302	5				7321			452	1		
	6286			011	1				7336			480	2		
	6292			649	3				7386			003	2		002
	6318			062	10				7393			793	2		791
	6430			155	1				7584			680	2		680
	6469			705	10			hf	7642			024	3		026
	6472			841	5				7802			651	2		
	6487			765	8				7881			320	1		
	6498			717	7			hf	7887			393	3		3898
	6521			508	2			hf	7967			342	3		341
	6533			159	7				8057			258	3		
	6543			360	4				8061			339	3		
	6554			196	3				8206			336	3		
	6595			561	7			hf	8231	633	3	6336	5		6348
	6632			464	4				8266			520	3		
	6666			965	6			hf	8280	116	5	1162	6		1163
	6668			920	10				8346	8217	3	822	3		823
	6678			972	3			hf	8409	1894	5	1894	4		190
	6681			036	3				8739			372	1		
	6728			008	10			hf	8819	4106	2	4113	5		412
	6827			315	9		315	hf	8952	2509	3	2506	8		254
	6846			613	3			hf	9045	4466	3	4460	7		446
	6866			838	1				9162	653	3	6520	7		654
	6872			107	3				9513			377	3		
	6882			155	5		1543		9799			697	5		
									9923			198	5		

WASHINGTON, June 20, 1934.

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PROPERTIES OF KNIT UNDERWEAR FABRICS OF VARIOUS CONSTRUCTIONS

By Charles H. Hamlin[1] and Ruby K. Worner

ABSTRACT

Knit underwear is made in a variety of weights, thicknesses, and constructions from cotton, wool, silk, rayon, and combinations of these fibers. Yet comprehensive data on the properties of underwear fabrics have not been available. The purpose of this paper is to supply data on representative underwear fabrics relative to the properties that appear to be important from the standpoint of comfort and health.

The thermal transmission, air permeability, thickness, weight, compressional characteristics, and coefficient of friction, measured under specified conditions, are recorded for 97 representative fabrics of given constructions and fiber compositions.

The interrelations between properties are shown graphically with the constructions and fiber compositions of the individual fabrics indicated. In general, the thermal transmission and air permeability of these fabrics varied inversely with thickness and with weight, the total compression varied directly with thickness, and the compressibility varied directly with density. The coefficient of friction was lowest for fabrics made from continuous filament silk and rayon yarns. It is evident, however, that when any one property is fixed, the other properties may be varied considerably.

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I. INTRODUCTION

The purpose of this paper is to record the results of measurements of thermal transmission, air permeability, thickness, weight, compressional characteristics, and coefficient of friction for a large variety of new unlaundered underwear fabrics under certain specified conditions. The fiber composition and details of construction of the fabrics are recorded and the interrelations between properties are shown graphically with the construction and fiber composition of the individual fabrics indicated. These measurements provide a line of attack on the problem of developing underwear with optimum properties as regards comfort and health.

[1] Research Associate at the National Bureau of Standards for the Underwear Institute..

This work was started several years ago as a cooperative study between the Underwear Institute (then the Associated Knit Underwear Manufacturers of America) and the National Bureau of Standards. The generous cooperation of the manufacturers who furnished the fabrics is gratefully acknowledged. The assistance of William D. Appel and H. F. Schiefer in the preparation of this paper is appreciated.

II. THE FABRICS

Ninety-seven underwear fabrics were examined. All of them were in commercial use for the manufacture of undergarments when the study was started. Ninety-four were of knit construction, 11 of them 2-layer fabrics, and 3 were of woven construction. The details of construction of the fabrics are given in table 1, in which the fabrics are arranged in the order of increasing thickness. The fabrics of the same thickness are listed in the order of increasing weight. Fabrics made from cotton; rayon; silk; wool; cotton and wool; rayon and silk; rayon and wool; silk and wool; cotton, rayon, and wool; and cotton, silk, and wool were included. Five types of knitting were represented; namely, plain (sometimes designated "circular flat knit"); rib; Rubenstein[2]; warp; and mesh. These constructions are illustrated in figures 1 (A to I).

[2] Edwin D. Fowle, *What is the Rubenstein Patent?* Textile World 78, 2814,(Dec. 13, 1930). See also U.S. Patent no. 1755968.

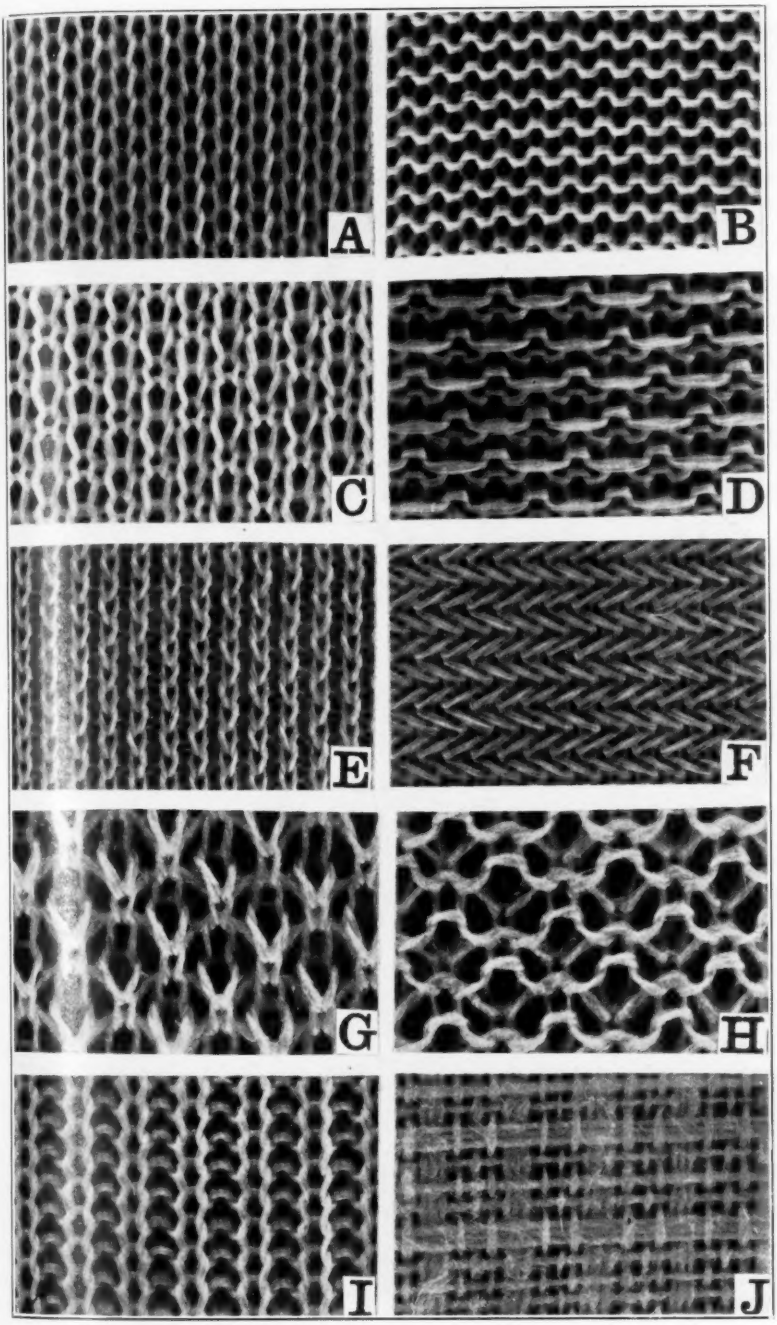

FIGURE 1.—*Types of interlacing.*

A. Plain knit, face.
B. Plain knit, back.
C. Rubenstein knit, face.
D. Rubenstein knit, back.
E. Warp knit, face.
F. Warp knit, back.
G. Mesh knit, face.
H. Mesh knit, back.
I. Rib knit, face, and back.
J. Woven, face, and back.

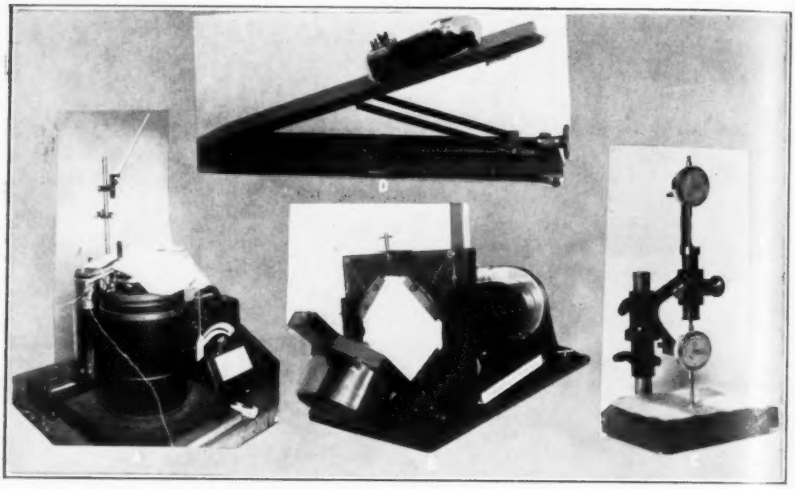

FIGURE 2.—*Equipment used for testing underwear fabrics for:*

A, Thermal transmission; *B*, air permeability; *C*, compressional characteristics; *D*, coefficient of friction.

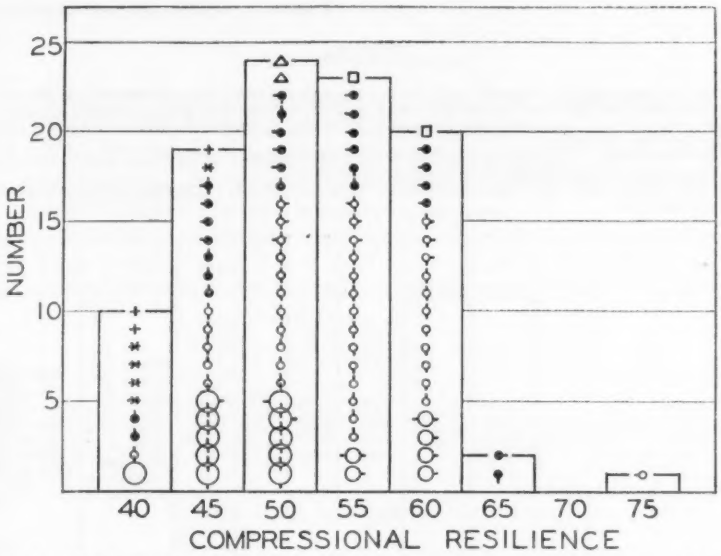

FIGURE 3.—*Distribution of fabrics with respect to compressional resilience (percent).*

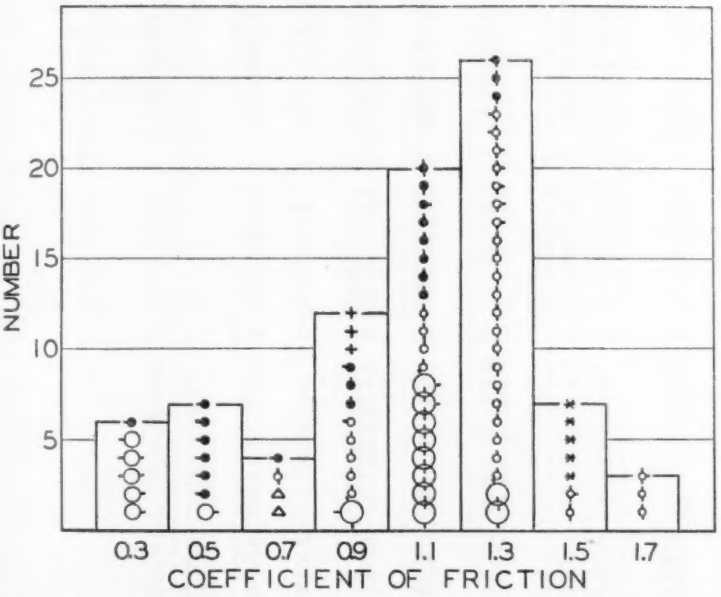

FIGURE 4.—*Distribution of fabrics with respect to coefficient of friction.*

TABLE 1.—*Details of construction and*

NOTES

Column

5 *Thermal transmission.*—Quantity of heat lost through the fabric when in contact on one side with a horizontal hot plate and on the other with still air, expressed in British thermal units per hour per square foot of fabric per degree Fahrenheit difference in temperature between the hot plate and the air above the fabric.

6 *Air permeability.*—Number of cubic feet of air perminute passing through 1 square foot of fabric, at a pressure drop across the fabric of 0.3 inches of water.

7 *Total compression.*—The change in thickness when the pressure is increased from 0.1 to 2.0 pounds per square inch.

1	2	3	4	5	6	7	8	9	10	11	12
Sample no.	Standard thickness	Weight	Density	Thermal transmission	Air permeability	Total compression	Compressibility	Compressional resilience	Coefficient of friction	Fiber: C=cotton, R=rayon, S=silk, s=spun, W=wool, w=weighted, numerals=contents %	Interlacing: f=fleeced, m=mesh knit, p=plain knit, r=rib knit, R=Rubenstein knit, w=warp knit
	In.	*Oz/yd²*	*Lb/ft³*			*In.*	*In²/lb*	*Percent*			
1	0.009	1.42	13.1	2.03	427	0.0030	0.13	58	0.4	S	w
2	.009	1.52	14.1	1.70	388	.0025	.13	57	.5	S	w
3	.010	2.06	17.2	1.91	517	.0025	.11	62	.3	Sw	w
4	.011	2.64	20.0	1.51	392	.0020	.08	62	.3	88R, 12S	w
5	.011	2.65	20.1	1.84	649	.0015	.05	60	.4	R	p
6	.011	2.65	20.1	1.62	586	.0015	.06	56	.5	R	p
7	.011	2.69	20.4	1.62	513	.0020	.08	54	-------	R	p
8	.012	2.39	16.6	1.54	453	.0025	.07	55	.2	85R, 15S	w
9	.012	2.89	20.1	1.88	547	.0015	.05	49	.4	R	p
10	.012	2.92	20.3	1.85	663	.0016	.06	46	.4	R	p
11	.012	2.97	20.6	2.17	152	.0030	.11	41	.9	C	woven
12	.013	3.77	24.2	2.07	489	.0020	.05	47	-------	R	p
13	.013	3.81	24.4	2.00	425	.0025	.08	53	-------	R	p
14	.014	3.00	17.9	1.42	455	.0020	.06	62	.4	R	w
15	.014	3.39	20.2	-------	671	.0015	.05	59	-------	R	p
16	.014	3.63	21.6	2.35	557	.0015	.05	59	.4	R	p
17	.014	3.87	23.0	1.67	491	.0015	.04	52	.5	R	p
18	.015	3.29	18.3	-------	635	.0020	.06	55	-------	R	p
19	.015	3.49	19.4	1.84	152	.0040	.10	46	1.0	C	woven
20	.016	2.98	15.5	1.45	451	.0055	.14	49	.7	Rs	p
21	.016	3.61	18.8	1.73	668	.0030	.10	60	-------	R	R
22	.016	4.02	20.9	1.99	537	.0020	.06	62	.5	R	p
23	.017	3.11	15.2	1.34	269	.0050	.11	67	1.1	Ss	p
24	.017	3.13	15.3	1.51	451	.0050	.11	55	1.0	Rs	p
25	.017	3.40	16.7	1.47	284	.0040	.10	48	1.1	C	p
26	.017	3.95	19.4	-------	593	.0040	.12	53	-------	R	R
27	.018	3.08	14.3	1.41	339	.0075	.14	47	1.1	C	p
28	.019	2.86	12.5	1.48	465	.0100	.19	66	1.2	W	p
29	.019	3.66	16.1	1.73	258	.0060	.11	42	1.0	C	p
30	.020	3.72	15.5	1.73	237	.0065	.12	41	1.1	C	p
31	.021	3.16	12.5	1.98	347	.0075	.14	44	.8	C	p
32	.022	2.77	10.5	1.70	550	.0100	.20	49	.8	C	m
33	.022	3.28	12.4	1.59	414	.0085	.15	49	.6	C	m
34	.022	3.53	13.4	1.46	319	.0085	.13	45	1.2	C	p
35	.023	3.13	11.3	1.56	524	.0105	.20	56	.8	C	p
36	.023	5.64	20.4	1.71	196	.0075	.11	46	1.1	32C, 37R, 31W.	p
37	.025	5.20	17.3	1.64	228	.0090	.14	52	1.2	29R, 71W	p
38	.026	4.00	12.8	1.56	319	.0070	.12	56	.9	C	r
39	.026	4.22	13.5	1.48	224	.0060	.10	53	1.0	C	r
40	.026	4.63	14.8	1.62	316	.0065	.10	61	1.3	C	r

NOTES—Continued

Column

8 *Compressibility.*—The ratio of the decrement in thickness to the increment in pressure for unit thickness at a pressure of 1 pound per square inch.

9 *Compressional resilience.*—The amount of work recovered from the specimen when the pressure is decreased from 2 to 0.1 pound per square inch, expressed as a percentage of the work done on the specimen when the pressure is increased from 0.1 to 2 pounds per square inch.

10 *Coefficient of friction.*—The tangent of the limiting angle between the inclined plane and the horizontal. See test procedure.

16 *Yarn number* (TYPP).—Number of thousand yarns per pound.

13	14	15	16	17		18
Finish: b=bleached, d=dyed, dr=dyed random, g=grey, m=mercerized	Wales or warp yarns per inch	Courses or filling yarns per inch	Yarn number (TYPP): C=cotton, CW=cotton and wool mixed, f=filling, R=rayon, S=silk, W=wool, w=warp	Twist—turns per inch: C=cotton, CW=cotton and wool mixed, f=filling, R=rayon, S=silk, w=warp, W=wool		Notes
				Single	Plied	
d	48	63				
d	46	64				
d	53	66				
d	42	55				
d	46	49	43.0	3		
d	46	49	41.5	4		
d	52	47	44.5	6		
d	44	57				
d	46	52	42.5	4		
d	47	52	42.5	4		
b	80	75	28.0w, 34.5f.	21w, 19f		
b	48	50	41.5	3		
d	39	48	30.0	6		
d	46	52				
d	38	43	29.0	3		
b	44	44	30.5	2		
d	43	46	28.5	4		
d	37	46	29.0	3		
g	80	75	28.0w, 34.5f	21w, 19f		
b	35	35	28.5	19		
d	38	42	28.5	3		
d	45	45	28.5	3		
b	39	36	30.0	8		
b	34	38	28.5	19		
bm	35	41	28.5	22	17	2-ply yarns.
d	41	37	29.0	3		
b	36	35	31.0	18		
b	37	35	31.5	20		
b	35	41	25.0	18		
b	34	43	25.5	19		
b	26	25	18.0	14		
bm	30	28	31.0	31	15	2-ply yarns.
b	32	22	30.5	20		
b	26	33	19.5	16		
g	25	26	18.0	14		
b	31	38	16.5	17CW, 3R		Single rayon and single cotton-and-wool yarn knit as 1 in each course.
b	35	36	18.5	13W, 4R		Single worsted and single rayon yarn knit as 1 in each course.
b	28	29	31.0	19		
b	28	29	27.5	18		
bm	29	32	27.5	22	16	2-ply yarns.

TABLE 1.—*Details of construction and*

1	2	3	4	5	6	7	8	9	10	11	12
Sample no.	Standard thickness	Weight	Density	Thermal transmission	Air permeability	Total compression	Compressibility	Compressional resilience	Coefficient of friction	Fiber: C=cotton, R=rayon, S=silk, s=spun, W=wool, w=weighted, numerals=contents %	Interlacing: f=fleeced, m=mesh knit, p=plain knit, r=rib knit, R=Rubenstein knit, w=warp knit
	In.	*Oz/yd²*	*Lb/ft³*			*In.*	*In²/lb*	*Percent*			
41	.026	5.21	16.7	1.56	750	.0040	.05	73	.9	R	r
42	.027	4.65	14.4	1.73	203	.0080	.11	52	1.2	C	r
43	.027	5.45	16.8	1.40	157	.0080	.12	49	1.2	71C, 29W	p
44	.028	5.78	17.2	1.23	192	.0130	.16	54	1.2	W	p
45	.030	4.36	12.1	1.28	240	.0070	.09	46	1.0	C	r
46	.034	5.06	12.4	1.37	390	.0110	.12	54	.8	C	r
47	.034	5.50	13.5	1.31	159	.0105	.13	48	1.3	C	r
48	.034	5.89	14.4	1.34	242	.0125	.14	48			
Face		3.41							1.0	71C, 29W	p
Back		2.48								C	p
49	.035	5.64	13.4	1.28	73	.0160	.17	40	.9	C	woven (twill)
50	.036	6.47	15.0	1.27	199	.0100	.10	53	1.2	63C, 28R, 9W	r
51	.036	6.50	15.0	1.48	216	.0090	.10	56	1.2	76C, 24W	r
52	.037	6.29	14.2	1.25	216	.0095	.10	61		59C, 41W	r
53	.037	6.35	14.3	1.20	269	.0130	.14	52			
Face		3.66							1.0	50C, 17Ss, 33W	p
Back		2.69								C	p
54	.037	7.12	16.0	1.32	146	.0090	.09	58	1.4	36C, 33Ss, 31W	r
55	.038	6.27	13.8	1.25	214	.0135	.14	47			
Face		3.52							1.1	72C, 28W	p
Back		2.75								C	p
56	.038	7.28	16.0	1.35	125	.0115	.11	52	1.3	80C, 10R, 10W	r
57	.038	7.48	16.4	1.39	177	.0115	.10	47	1.6	76C, 24W	r
58	.038	7.71	16.9	1.45	253	.0135	.14	49			
Face		4.72							.9	37C, 40R, 23W	p
Back		2.99								C	p
59	.038	8.55	18.8	1.40	96	.0090	.09	53	1.4	40C, 25Ss, 35W	r
60	.039	6.52	13.9	1.38	192	.0145	.14	46			
Face		3.88							1.1	34C, 32Ss, 34W	p
Back		2.64								C	p
61	.039	7.00	15.0	1.30	190	.0115	.10	58	1.4	41S, 59W	r
62	.039	8.07	17.2	1.95	135	.0095	.09	52	1.3	72C, 28W	r
63	.040	7.20	15.0	1.14	163	.0105	.10	53	1.3	69C, 31W	r
64	.040	8.67	16.8	1.34	118	.0095	.09	52	1.7	36C, 33Ss, 31W	r
65	.041	8.52	17.3	1.43	90	.0110	.09	48	1.4	71C, 29W	r

properties of underwear fabrics—Continued

13	14	15	16	17		18
Finish: b=bleached, d=dyed, dr=dyed random g=grey, m=mercerized	Wales or warp yarns per inch	Courses or filling yarns per inch	Yarn number (TYPP): C=cotton, CW=cotton and wool mixed, f=filling, R=rayon, S=silk, W=wool, w=warp	Twist—turns per inch: C=cotton, CW=cotton and wool mixed, f=filling, R=rayon, S=silk, w=warp, W=wool		Notes
				Single	Plied	
d	30	40	29.0	3	------	
b	30	29	24.5	17	------	
b	32	35	16.0	12CW, 23C	------	Single cotton-and-wool yarn and single cotton yarn knit as 1 in each course.
b	33	40	17.5	15	8	2-ply worsted yarns.
b	27	32	27.5	16	------	
g	27	31	25.5	19	------	
b	32	27	26.5	17	------	
bm	27	25	26.0C, 18.5 CW	24 12	16 ------	2-layer fabric. 1 course with 2-ply mercerized cotton yarn alternating with 2 courses single cotton-and-wool yarn.
b	26	25	25.5	26	24	2-ply yarns.
b	78	42	19.5w, 10.5f.	23w, 12f	------	Filling yarns were napped.
b	23	31	17.0	12CW, 21C, 2R.	------	2 courses with single cotton-and-wool yarn alternating with 2 courses containing a single cotton and a single rayon yarn knit as 1 in each course.
dr	24	38	18.0	15C, 9W	------	Alternate courses of single cotton and single worsted yarns.
dr	26	33	25.0	25C, 15CW	------	2 single yarns, 1 of cotton, and 1 of cotton-and-wool knit as 1 in each course.
b	27	26	25.5S 16.0CW	17 11	13 ------	2-layer fabric. 1 course of 2-ply spun silk yarn alternating with 3 courses single cotton-and-wool yarn.
b	27	26	24.5	26	24	2-ply yarns.
b	25	33	17.5	14CW, 12S	------	2 single yarns, 1 of cotton-and-wool, and 1 of spun silk, knit as 1 in each course.
bm, dr	26	29	26.5C 17.0CW	26 14	16 ------	2-layer fabric. 1 course of 2-ply cotton yarn alternating with 2 courses of single cotton-and-wool yarn.
b	26	29	25.5	28	23	2-ply yarns.
b	27	29	15.0C&R 18.0CW	15C, 2R 11	------ ------	5 courses of single cotton-and-wool yarns alternating with 1 course containing 2 single yarns, 1 of cotton and 1 of rayon knit as 1 yarn.
bm	26	32	17.5CW 18.0C	14 19	------ 13	3 courses of single cotton-and-wool yarns alternating with 3 courses of 2-ply mercerized cotton yarns.
b	26	25	17.5C&R 16.5CW &R	22C, 2R 14CW, 4R	------ 4	2-layer fabric. 1 course of 2 single yarns, 1 of cotton and 1 of rayon, knit as 1, alternating with 3 courses of 2-ply yarns composed of a single cotton-and-wool and a single rayon yarn.
b	26	25	27.0	24	24	2-ply cotton yarns.
b	23	29	13.0	14CW, 10S	------	2 single yarns, 1 of cotton-and-wool and 1 of spun silk, knit as 1.
b	26	27	17.0	13CW, 11S	6	2-layer fabric. 2-ply yarns, composed of 1 single cotton-and-wool and 1 single spun silk yarn.
b	26	27	25.0	28	22	2-ply cotton yarns.
b	26	37	21.5	16W, 10S	------	2 single yarns, 1 of worsted and 1 of spun silk, knit as 1.
b	25	34	17.5	14CW, 22C	------	2 single yarns, 1 of cotton-and-wool and 1 of cotton, knit as 1.
b	25	28	16.0	12CW, 18C	------	2 single yarns, 1 of cotton-and-wool and 1 of cotton, knit as 1.
b	28	35	17.0	12CW, 11S	------	2 single yarns, 1 of cotton-and-wool and 1 of spun silk, knit as 1.
b	27	34	16.5	16CW, 19C	------	2 single yarns, 1 of cotton-and-wool and 1 of cotton, knit as 1.

TABLE 1.—*Details of construction and*

1	2	3	4	5	6	7	8	9	10	11	12
Sample no.	Standard thickness	Weight	Density	Thermal transmission	Air permeability	Total compression	Compressibility	Compressional resilience	Coefficient of friction NN6N	Fiber: C=cotton, R=rayon, S=silk, s=spun, W=wool, w=weighted, numerals=contents %	Interlacing. f=fleeced, m=mesh knit, p=plain knit, r=rib knit, R=Rubenstein knit, w=warp knit
	In.	*Oz/yd²*	*Lb/ft³*			*In.*	*In³/lb*	*Percent*			
66	.043	6.94	13.4			.0130	.11	50	1.2	36C, 32Ss, 32W.	r.
67	.043	7.78	15.1	1.42	96	.0120	.11	44	1.3	C	r.
68	.043	9.12	17.7	1.60	76	.0105	.09	50	1.3	78C, 22W	r.
69	.044	6.95	13.2	1.35	209	.0135	.12	60	1.4	36Ss, 64W	r.
70	.044	8.15	15.4	1.37	168	.0120	.10	56	1.3	37Ss, 63W	r.
71	.044	8.44	16.0	1.66	120	.0095	.09	54	.8	67C, 33W	r.
72	.045	7.20	13.3	1.43	216	.0150	.13	53	.9	C	r.
73	.045	8.10	15.0	1.32	162	.0160	.14	48			
Face		3.97							1.1	61C, 39W	p.
Back		4.13								C	p.
74	.046	7.21	13.1	1.31	139	.0180	.14	44			
Face		3.67							1.1	81C, 19W	p.
Back		3.54								C	p.
75	.046	7.39	13.4	1.23	153	.0170	.12	58	1.2	37C, 63W	r.
76	.046	8.79	15.9	1.31	102	.0120	.09	46	1.4	70C, 30W	r.
77	.047	7.85	13.8	1.11	153	.0180	.14	48			
Face		3.99							1.2	30C, 70W	p.
Back		3.86								C	p.
78	.047	8.34	14.8	1.29	210	.0175	.14	44			
Face		4.20							1.2	83C, 17W	p.
Back		4.14								C	p.
79	.048	7.80	13.5	1.03	144	.0195	.15	43			
Face		3.81							1.1	61C, 39W	p.
Back		3.99								C	p.
80	.048	8.27	14.4	1.29	194	.0150	.11	58	1.3	W	r.
81	.050	8.44	14.1	1.13	130	.0165	.13	42			
Face		4.32							1.0	52C, 48W	p.
Back		4.12								C	p.
82	.053	10.08	15.8	1.28	96	.0175	.12	48		C	r.
83	.056	11.90	17.7		78	.0130	.10	52		99C, 1W	r.
84	.058	10.28	14.8	1.14	143	.0150	.11	57		92C, 8W	r.
85	.061	11.85	16.2	1.34	55	.0160	.10	40	1.3	C	r.
86	.062	11.60	15.6	1.34	96	.0175	.10	57	1.0	36C, 64W	r.
87a	.063	8.00	10.6	.92	249	.0205	.14	56		W	r.
87b	.048	6.66	11.6			.0175	.13	59		W	r.
88a	.064	8.20	10.7	1.03	157	.0230	.14	55	1.4	W	r.
88b	.049	7.16	12.2			.0170	.13	61		W	r.
89	.064	11.32	14.7	1.20	96	.0225	.13	48	1.1	95C, 5W	r.
90	.066	12.02	15.2	1.03	159	.0195	.12	62	1.4	40C, 60W	r.

properties of underwear fabrics—Continued

13	14	15	16	17		18
Finish: b=bleached, d=dyed, dr=dyed random, g=grey, m=mercerized	Wales or warp yarns per inch	Courses or filling yarns per inch	Yarn number (TYPP): C=cotton, CW=cotton and wool mixed f=filling, R=rayon, S=silk, W=wool, w=warp	Twist—turns per inch: C=cotton, CW=cotton and wool mixed, f=filling, R=rayon, S=silk, w=warp, W=wool		Notes
				Single	Plied	
b	23	33	16.5	15CW, 11S	.....	2 single yarns, 1 of cotton-and-wool and 1 of spun silk, knit as 1.
b	20	26	12.0	9	.....	
b	22	29	13.5	13CW, 17C	.....	2 single yarns, 1 of cotton-and-wool and 1 of cotton, knit as 1.
b	21	30	17.0	9S, 12W	.....	2 single yarns, 1 of spun silk and 1 of worsted knit as 1.
b	23	37	16.0	9S, 13W	.....	2 single yarns, 1 of spun silk and 1 of worsted, knit as 1.
b	23	31	13.5	15C, 12CW	.....	2 single yarns, 1 of cotton and 1 of cotton-and wool, knit as 1.
g	17	25	12.0	9	.....	2-layer fabric.
b	25	26	16.5	12	.....	Single cotton-and-wool yarns.
b	25	26	17.0	15	.....	2-layer fabric.
b	26	27	16.5	12	.....	Single cotton-and-wool yarns.
b	25	27	17.5	15	.....	
b	26	32	19.0	23C, 14W	.....	2 single yarns, 1 of cotton and 1 of wool, knit as 1.
dr	26	36	16.0	16CW, 22C	.....	2 single yarns, 1 of cotton-and-wool and 1 of cotton, knit as 1.
m	26	28	17.0C	20	13	2 layer fabric. 1 course of 2-ply mercerized cotton yarn alternating with 3 courses of single cotton-and-wool yarn.
b	.....	.....	17.0CW	13	.....	
b	26	27	17.0	16	.....	2-layer fabric.
dr	24	28	17.0	14	.....	
b	24	28	18.0	14	.....	2-layer fabric.
dr	26	26	17.5	14	.....	
b	26	27	18.0	15	.....	
b	23	36	16.0	14	.....	Each course consists of 2 single worsted yarns knit as 1.
dr	26	26	15.5	10	.....	2-layer fabric.
b	26	26	14.5	11	.....	
b	20	26	10.0	8	.....	Back of fabric is brushed.
dr	18	21	7.5C 7.5 C & CW	8 9C, 16CW	.....	7 courses of single cotton yarns, alternating with 1 course composed of a single cotton and a single cotton-and-wool yarn knit as 1. Back of fabric is slightly brushed.
dr	15	18	8.5C 13.5 C & CW	8 18C, 16CW	.....	1 course of single cotton yarn, alternating with 1 course composed of a single cotton and a single cotton-and-wool yarn knit as 1. Back of fabric is slightly brushed.
b	18	32	9.5	8	.....	
b	18	28	8.0	15C, 11W	.....	2 single yarns, 1 of cotton and 1 of worsted, knit as 1.
dr	15	29	17.5	14	.....	Each course consists of 2 single worsted yarns knit as 1. "a" is relatively loosely knit compared to "b."
dr	21	32	17.5	14	.....	
b	16	25	17.0	18	.....	Each course consists of 2 single worsted yarns knit as 1. "a" is relatively loosely knit compared to "b."
b	24	31	17.0	18	.....	
dr	18	25	7.5	6	.....	Back of fabric is slightly brushed.
dr	17	21	7.0	12C, 9W	.....	Each course consists of 2 single yarns, 1 of cotton and 1 of worsted, knit as 1.

TABLE 1.—*Details of construction and*

1	2	3	4	5	6	7	8	9	10	11	12
Sample no.	Standard thickness	Weight	Density	Thermal transmission	Air permeability	Total compression	Compressibility	Compressional resilience	Coefficient of friction	Fiber: C=cotton, R=rayon, S=silk, s=spun, W=wool, w=weighted, numerals=contents %	Interlacing: f=fleeced, m=mesh knit, p=plain knit, r=rib knit, R=Rubenstein knit, w=warp, knit
	In.	*Oz/yd²*	*Lb/ft²*			*In.*	*In³/lb*	*Percent*			
91	.067	8.36	10.4	1.01	117	.0395	.21	45	1.5	C	pf
92	.067	11.34	14.1	1.17	67	.0270	.15	47	1.6	78C, 22W	r
93	.077	10.19	11.0	1.06	120	.0275	.14	62	1.2	W	r
94	.083	9.72	9.8	.86	88	.0430	.21	42	1.6	C	pf
95	.088	11.70	11.1	.86	67	.0452	.19	42	1.5	C	pf
96	.092	10.98	9.9	.66	74	.0530	.23	42	1.4	C	pf
97	.095	11.00	9.6	.72	57	.0525	.23	38	1.4	C	pf

properties of underwear fabrics—Continued

13	14	15	16	17		18
Finish: b=bleached, d=dyed, dr=dyed random, g=grey, m=mercerized	Wales or warp yarns per inch	Courses or filling yarns per inch	Yarn number (TYPP): C=cotton, CW=cotton and wool mixed f=filling, R=rayon, S=silk, W=wool, w=warp	Twist—turns per inch: C=cotton, CW=cotton and wool mixed, f=filling, R=rayon, S=silk, w=warp, W=wool		Notes
				Single	Plied	
dr	21	22	12.0	20g, 19dr		Each course consists of 2 single yarns and a backing yarn, knit as 1. Size of backing yarn unknown.
b	14	19	5.5	6		
b	16	30	8.0	7		
dr	19	26	12.5	21g, 21dr		Each course consists of 2 single yarns, and a backing yarn, knit as 1. Size of backing yarn unknown.
dr	23	20	12.5	18g, 23dr		Each course consists of 2 single yarns and a backing yarn, knit as 1. Size of backing yarn unknown.
dr	21	25	12.5	17g, 19dr		Each course consists of 2 single yarns and a backing yarn knit as 1. Size of backing yarn unknown.
dr	23	28	13.0	18g, 20dr		Each course consists of 2 single yarns and a backing yarn knit as 1. Size of backing yarn unknown.

The two-layer fabrics consisted of a "back" fabric composed entirely of cotton, and a "face" fabric composed of a single kind of fiber or a combination of fibers. (The term "back" is used in this paper to refer to the surface of the cloth that would normally be worn next to the body, while "face" designates the surface of the cloth that would normally be the outside surface when worn). The two layers are knit simultaneously and are joined together at regular intervals by having the yarn of the back fabric knit into the face fabric.

The yarns in the fabrics varied in size or "number" from 5 to 45,000 yd/lb,[3] and differed also with respect to the number of plies and the number of turns of twist per inch.

Some of the fabrics were in the grey state (i.e., not processed beyond knitting or weaving), others were bleached, dyed, or mercerized. Some were brushed or fleeced.

Two of the woven fabrics, numbers 11 and 19, were typical of the light weight cotton cloths used for men's union suits and are similar in weight and thickness to some of the knit fabrics. The weave is shown in figure 1(J). It is a small checked design in which 3 yarns are woven as 1 for every fourth yarn in both the warp and the filling. The third woven fabric, number 49, is a medium weight 3/1 twill weave cloth with a light nap on one side. It is similar in thickness and weight to some of the knit fabrics and is therefore of interest for comparison.

III. METHODS OF TEST

All fabrics were conditioned for test by exposure to an atmosphere of 65 ± 1 percent relative humidity and 70° to 80° F temperature. The tests were conducted under these conditions.

(a) THERMAL TRANSMISSION

The apparatus [4] developed by Schiefer, shown in figure 2(A), was used for measuring the transmission of heat through the fabrics. The

[3] The TYPP system for designating the size or "number" of the yarn is used in this paper because of its convenience for comparing the sizes of the yarns of different fiber composition. The yarn number is the number of thousands of yards per pound of the yarn. This system was recently sponsored by E. D. Fowle in Textile World, 81,1470(Apr. 23, 1932).

[4] This apparatus was described briefly in the Bureau of Standards Technical News Bulletin no. 166, p. 15, (February 1931). An iron disk, painted with black lacquer, fits into the opening of a vacuum (thermos) jar. The disk is heated by means of a helical coil placed below it in the jar. A cavity in the disk is connected with a capillary and is filled with mercury which expands and contracts as the disk is heated or allowed to cool. The fluctuating mercury column in the capillary makes or breaks an electrical contact in a circuit which, operating through a relay, throws the current off or on in the heating coil and thus maintains the disk at a temperature which is maintained constant during the test to within ±0.1° F.

The specimen to be tested is clamped over the disk with the upper surface exposed to the standard atmosphere. The temperature of the standard atmosphere during a test is maintained constant to within ±0.2° F. The temperature of the upper surface of the disk is measured with a thermocouple. When a steady state of thermal equilibrium is established within the vacuum jar, that is, when there is no progressive change in the temperature of the disk, the test is begun. The intervals during which the current in the heating coil is off and on are timed with stop watches. Usually 10 current-off and 10 current-on intervals are taken for a test. The total time of a test usually varies between 20 and 30 minutes. The current indicated by an ammeter and the room temperature are recorded at frequent intervals during a test. The quantity of heat supplied to the vacuum jar per unit time per degree difference in temperature during a test is computed from the expression $\frac{K I^2 \epsilon t_c}{[\epsilon t_c + \epsilon t_o] T}$ where I denotes the current; t_c, a current-on interval; t_o, a current-off interval; T, the average temperature difference between the upper surface of the disk and the room; and K, a constant which includes the resistance of the heating coil and factors for expressing the result in convenient units. Part of the heat input is dissipated through the specimen and the remaining part is lost through the apparatus. This end loss through the apparatus was determined for a thick layer of cork of known thermal conductivity in conjunction with a number of fabrics. It was found to increase linearly with the gross heat input, the increase being about 10 percent for a 100 percent increase in the gross input. A correction for end loss, depending upon the gross heat input, was applied to the gross heat input for each fabric. This value divided by the area of the disk is the quantity of heat transmitted per unit time per unit area of fabric per degree difference in temperature.

value reported is the quantity of heat passing through 1 ft^2 of fabric in 1 hour for each degree difference in temperature between a horizontal black hot plate and the air above the fabric when one side of the fabric is in contact with the hot plate and the other side is in contact with still air. The temperature of the hot plate for the values reported was maintained at 102 $\pm 2°$ F, approximately body temperature.

(b) AIR PERMEABILITY

The air permeability of the fabrics was measured with the apparatus developed by Schiefer and Best,[5] shown in figure 2(B). The fabric is clamped between two orifice rings under a slight tension and air is drawn through it and through a calibrated orifice by means of a suction fan. The drop in pressure across the fabric and that across the orifice is observed. From this is calculated the rate of air flow through the fabric at a given pressure drop across it. Each value in the table is the number of cubic feet of air passing through 1 ft^2 of the fabric in 1 minute when the air pressure on the one side of the fabric is equivalent to that of 0.3 in. of water above that on the other side.

(c) THICKNESS AND COMPRESSIONAL CHARACTERISTICS

The "standard thickness", "total compression", "compressibility", and "compressional resilience" of the fabrics were measured with the compressometer shown in figure 2(C), according to the method devised by Schiefer.[6] These properties appear to be useful criteria of the "handle" or "feel" of fabrics when they are squeezed between the fingers and are related to what are commonly designated as softness and springiness of underwear fabrics, which may be important attributes.

In this test, the specimen is placed between the plane parallel surfaces of the anvil and the presser foot, which is a circular disk, 1 inch in diameter. Pressure is applied gradually through the foot by turning the knob at the side of the instrument. The pressure on the specimen is indicated by the upper dial, and the corresponding distance between the presser foot and the anvil, that is, the thickness of the specimen at this pressure, is indicated by the lower dial. When the pressure reaches 2 lb/in.^{2} the knob is turned in the opposite direction and the pressure on the specimen is thus gradually released. The thickness is observed at a series of increasing and decreasing pressures.

The thickness of a knit underwear fabric is purely a matter of definition. The "standard thickness" reported here is the distance between the plane parallel surfaces of the anvil and the presser foot of the thickness gage when the pressure on the specimen has been gradually increased to 1 lb/in^2 The total "compression" is by definition the change in thickness when the pressure is increased from 0.1 to 2.0 lb/in.^{2} The "compressibility" is the ratio of the decrement in thickness to the increment in pressure for unit thickness at a pressure of 1 lb/in.^{2} The "compressional resilience" is the amount of work recovered from the specimen when the pressure is decreased

[5] Herbert F. Schiefer and Alfred S. Best, *A portable instrument, for measuring air permeability of fabrics.* B.S.J. Research **6**, 51(1931); RP261.

[6] Herbert F. Schiefer, *The compressometer, an instrument for evaluating the thickness, compressibility, and compressional resilience of textiles and similar materials.* B.S. J.Research **10**,705(1933); RP561.

from 2.0 to 0.1 lb/in^2 expressed as a percentage of the work done on the specimen when the pressure is increased from 0.1 to 2.0 lb/in.^{2}

(d) COEFFICIENT OF FRICTION

The coefficient of friction between two pieces of the same material was tested with Mercier's equipment [7] (fig. 2D) which employs the principle of the inclined plane. The faces of two pieces of the same fabric were opposed on the inclined plane and sliding block with the ribs or wales running parallel to the direction of motion. These conditions were selected because they represent the usual direction in which outer clothing is pulled over underclothing.

It is recognized of course that the value obtained depends upon whether the face or back of the fabric is tested and the orientation with reference to the direction of the wales and courses; also that a different series of values would be obtained if the fabrics were tested against a second or "standard" fabric. Since the coefficient of friction depends on the nature of the materials and the smoothness of the surfaces, it is to be presumed that in such a series, the various fabrics would be found in the same sequence.

IV. DISCUSSION OF RESULTS

It is obvious that no one set of test conditions will simulate all conditions of use of underwear fabrics. Most of the fabrics studied are easily stretched and will change materially in thickness, weight per unit area, and in surface characteristics with movements of the wearer of garments made from them. The conditions of test used in this work are more or less standard in textile testing laboratories. The interpretation of the results in terms of the use of the fabrics is definitely limited by the test conditions and much work is needed before a clear picture can be drawn. However, in general, two fabrics which differ significantly in a property in the test used are expected to differ in a similar way though perhaps to a different degree under some other set of conditions. Exceptions to this statement are to be expected, but a consideration of the nature of the particular fabric and the changes in the test conditions will usually explain if not anticipate the exceptional results. It is believed that the range in properties of the group of fabrics will not be materially changed by measurements conducted under other conditions or by modifications of the fabrics brought about by laundering.

The results of this study are summarized in table 1. Since the thinnest and lightest-weight fabrics are usually made of continuous filament silk or rayon yarns, it is not surprising to find them grouped together in the fore part of the table. These are followed by the fabrics composed of spun silk or spun rayon fibers, then by those made from cotton, wool, or mixtures of fibers, and finally by the fleece-lined fabrics.

The results given in the table show that, in general, increasing thickness is accompaied by increasing weight, decreasing air permeability, and decreasing thermal transmission, as was to be expected from experience and from the findings of other investigators. However, very precise correlation between these different factors is not to be expected in a series of fabrics such as this one in which the different

[7] Alfred A. Mercier, *Coefficient of friction of fabrics.* B.S. J. Research 5, 243(1930); RP196.

materials are simply representative of those on the market. Most valuable studies could be made by constructing series of fabrics in which only one element is varied.

The properties of fabrics numbers 20, 23, 24, 27, and 28 are particularly interesting for these fabrics were knit on the same machine from yarns of approximately the same size, but of different fiber compositions. The values for the thermal transmission are practically the same except for fabric number 23, of spun silk which has a comparatively low value. This fabric is made from yarn of relatively low twist which may account in part at least for this difference and also for the fact that it has the lowest air permeability of the five fabrics. It will be noted that fabric number 23 has a slightly greater number of wales per inch than the other fabrics in this series. The differences in air permeability may be in part attributable to the differences in the ability of the fabrics to stretch which is evident on handling them. A small tension is applied to the fabrics during this test, and doubtless some of them stretched more than others. The wool fabric, number 28, is the thickest and lighest of the series, has an appreciably greater total compression, and is more compressible than any of the other fabrics, due no doubt to the resilience of the wool fiber.

Fabrics numbers 30 and 35 were similar, except that the former was bleached and the latter was in the grey state. For these particular fabrics, bleaching increased the thermal transmission and decreased the permeability to air, total compression, compressibility, and compressional resilience.

In order to show more clearly the interrelations of the properties of the knit fabrics, a number of charts are presented. Different symbols are used in the charts to designate the type of interlacing of the yarns and the fiber compositions so that the effects of these characteristics may be noted.

The thickness and weight of each fabric is plotted in figure 5. In a general way, these properties are proportional to each other for all the fabrics except the fleece lined and three of the wool rib knit fabrics which are relatively thick for their weight.

The air permeability is plotted against the thermal transmission in figure 6. This chart indicates that for any specific air permeability, considerable variation in thermal transmission is possible and vice versa.

The thermal transmission and air permeability of each fabric is plotted against its thickness and its weight in figure 7. In general, both thermal transmission and air permeability are relatively high for the thin or light fabrics and relatively low for the thick or heavy fabrics. It is clear, however, that fabrics having a given thickness or weight can be made in a considerable range of either thermal transmission or air permeability. The tendency for several of the types of fabrics tested to be grouped together in these figures will be noted. It will also be observed that the warp knit fabrics tested are in general less permeable to air than plain knit fabrics of comparable thickness but slightly greater weight. The values for the thermal transmission of these fabrics cover a relatively wide range which is comparable for the two types. With one exception, the fleece-lined fabrics are the thickest fabrics tested and have lower values for thermal transmission than other fabrics of comparable weights. They are grouped with rib-knit fabrics of similar weights with respect to air permeability.

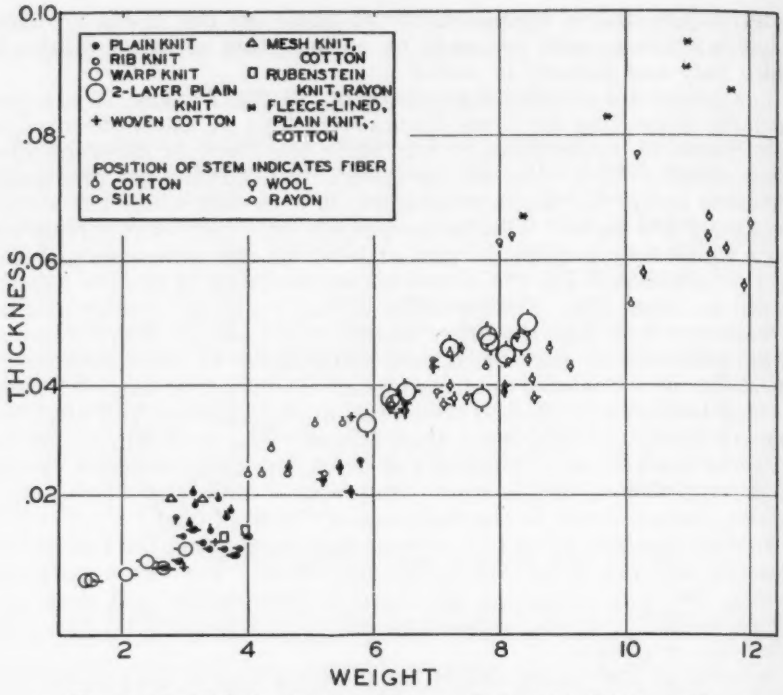

FIGURE 5.—*Relation between thickness (in.) and weight (oz/yd²).*

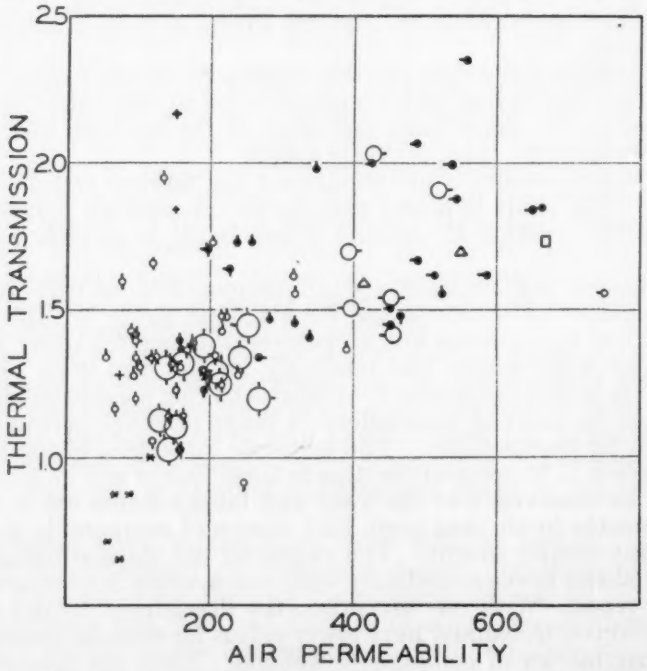

FIGURE 6.—*Relation between thermal transmission (Btu/hr ft² F) and air permeability (ft³/min ft², at pressure drop of 0.3 in. water).*

Figures 8, 9, and 3, (p. 313), show some relationships of the compressional characteristics of the fabrics. Total compression correlates well with thickness, figure 6, for the whole group of fabrics, and even better when the fabrics of similar construction are compared; for example, the

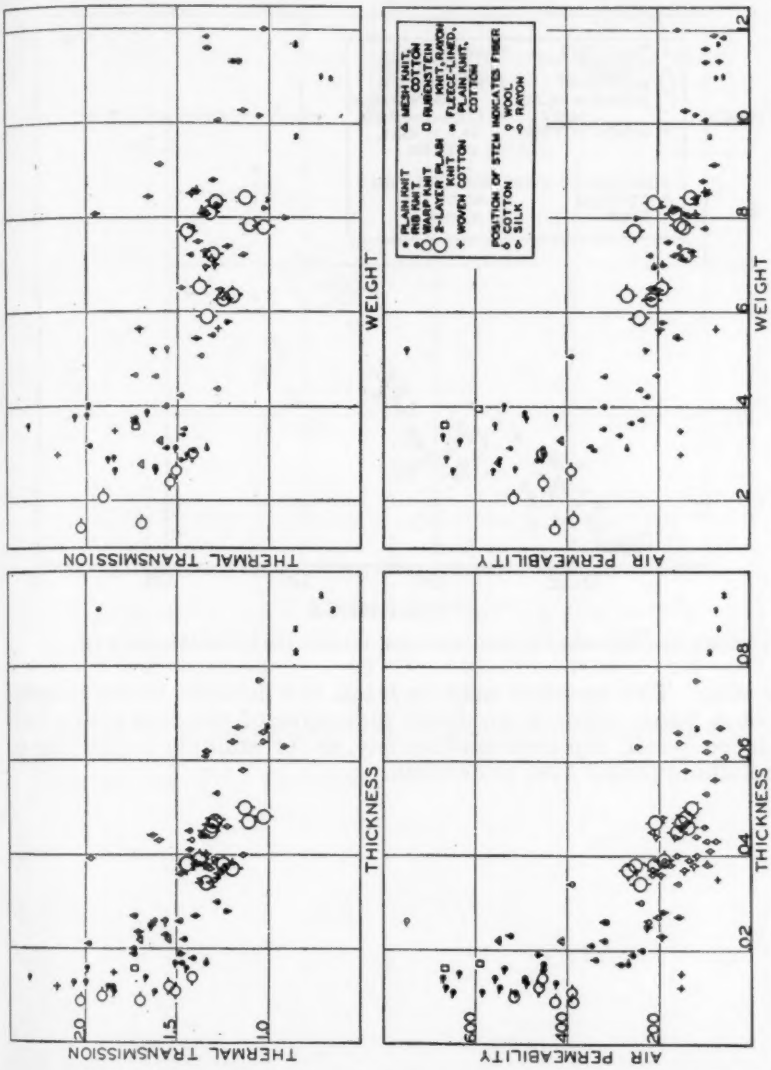

FIGURE 7.—*Thermal transmission (Btu/hr ft² F) and air permeability (ft³/min ft², at pressure drop of 0.5 in. water) in relation to thickness (in.) and weight (oz/yd²).*

group of fleece-lined fabrics, the two-layer fabrics, the rib-knit fabrics. The compressibility decreases with increasing density (i.e., the weight in pounds of 1 cubic foot of fabric based on the standard thickness) figure 9, though for any value of either property, there are fabrics having a range of values with respect to the other property. The compressional resilience of the majority of the fabrics lies between 45 and 60 percent, figure 3.

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The distribution of the fabrics with respect to coefficient of friction between two pieces of the same fabric when the faces are opposed is shown in figure 4, (p. 313). As was to be expected, the fabrics made from the continuous filament silk or rayon yarns have the lowest coefficient

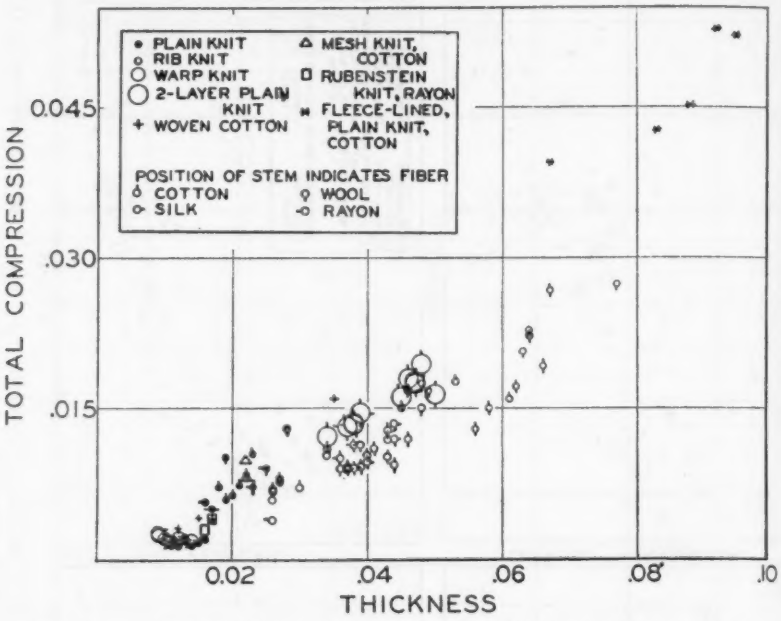

FIGURE 8.—*Relation between total compression (in.) and thickness (in.).*

of friction. This property may be taken as a measure of the smoothness of a fabric, which is no doubt indicative of the ease with which that fabric would slip over another one, as for example in the case of outerclothing pulled over underclothing.

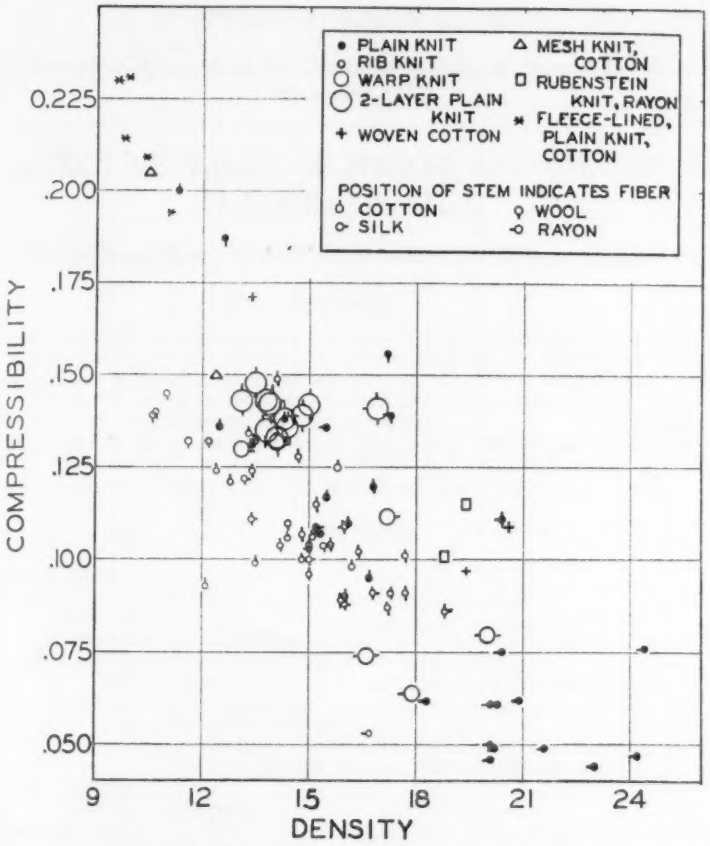

FIGURE 9.—*Relation between compressibility* (in^2/lb) *and density* (lb/ft^3).

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PROTECTIVE VALUE OF NICKEL AND CHROMIUM PLATING ON STEEL

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ABSTRACT

Exposure tests of plated steel were conducted in cooperation with the American Electroplaters' Society and the American Society for Testing Materials, in rural, suburban, industrial, and marine locations. It was found that the thickness of the nickel layer is more important than any other factor. An intermediate layer of copper decreases the protective value of thin deposits but is not detrimental in thick coatings, especially if they are chromium plated. The customary thin chromium coatings (0.00002 in. or 0.0005 mm) increase the resistance to tarnish, but not the protection against corrosion.

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I. INTRODUCTION

In order to determine the relative protective values of different electroplated coatings on steel, exposure tests were conducted during the past 2 years through cooperation of the American Electroplaters' Society and American Society for Testing Materials with the National Bureau of Standards. The details of the experiments and inspections were arranged by a joint committee. The experimental work was conducted at the Bureau by the Research Associate of the American Electroplaters' Society with the assistance of various members of the Bureau staff.

This report is confined to those coatings in which the outer layer was nickel or chromium, sometimes with intermediate layers of copper, and occasionally of zinc or cadmium. Specimens plated only with zinc or cadmium were exposed simultaneously, but as these have thus far shown failure in only three locations, the results will be reserved for later publication.

As part of this investigation, accelerated tests and their relation to the results of atmospheric corrosion were studied. A study was also made of methods for stripping electro-deposited coatings to determine their weight and average thickness. The results of these investigations will be published in later papers.

II. PREPARATION OF SPECIMENS

1. BASE METAL

The base metal was cold-rolled strip steel with a selected good finish, which required no polishing. It was 4 in. (10 cm) wide [2] and 0.031 in. (0.78 mm) thick (U.S. Gage no. 22). The steel was SAE. no. 1010 which contains approximately 0.1 percent of carbon. The specimens were each 4 by 6 in. (10 by 15 cm). Microscopical examinations of the steel before and after plating, and after exposure, failed to detect any inclusions or structural defects that might affect the quality or protective value of the plated coatings. A few strips were rejected that showed, after pickling or plating, some rolling lines with slag inclusions.

Each specimen was numbered near one corner with a steel die, and a narrow strip was cut half-way across the top edge and turned over at a right angle to serve as a hanger. Six specimens were mounted in the same plane in a steel rack so that there was about 0.25 in. space between each edge and the adjoining plate or portion of the rack. Tests showed that with this spacing the maximum variation from the average weight of coatings on the 12 specimens plated on 2 racks in one operation was less than 5 percent, and the mean variation was

[2] Most of the experimental work was conducted with metric measurements. However, as the thickness of the coatings was specified in fractions of an inch, the English units of thickness have been used in this paper, in some cases with metric equivalents. The conversions are in all cases approximate, as no high precision was involved

about 2 percent. Microscopical examination of cross sections showed that close to the edge the thickness of the coatings was about 50 percent greater than the nominal thickness, but that on over 90 percent of the area the variations were less than 10 percent from the average thickness.

2. PREPARATION FOR PLATING

In both the cleaning and plating processes, a certain convenient procedure was arbitrarily selected as a standard. This designation does not imply that it was superior, but merely that it served as a basis of comparison.

The preparation consisted essentially in the removal of grease, which process is designated by platers as "cleaning", and treatment with acid, that is, pickling. Although there was no need for pickling to remove visible oxide or scale from this steel, preliminary tests showed that definite etching of the steel was necessary to insure good adherence of the deposits, as measured in tests that involved bending, elongation, and extrusion in the Erichsen test.

Standard cleaning "A".[3] Each plate was subjected to the following treatments.

"1". The bulk of the grease was removed with either carbon tetrachloride or amyl acetate. The plates were then:

"2". Cleaned electrolytically as cathodes at about 90 C (194 F) and 5 amp/dm^2 (47 amp/ft^2) for 5 minutes in a solution with the composition shown below.

Alkaline cleaning solution	Approx. *N*	g/l	oz/gal
Sodium carbonate, Na_2CO_3	0.6	30	4
Trisodium phosphate, $Na_3PO_4.12H_2O$	0.25	30	4
Sodium hydroxide, NaOH	0.2	7.3	1

"3". Scrubbed with a bristle brush that was wet with the same cleaning solution;

"4". Rinsed in hot water;

"5". Pickled for 2 minutes in 2 *N* sulphuric acid (98 g/l or 13 avdp oz/gal or 7.5 fl oz/gal of H_2SO_4) at 50 C (122 F); and

"6". Rinsed in cold water.

Cathode pickling "B". The procedure was the same as in "A", except that *instead* of step "5" the steel was pickled *cathodically* in 2 *N* sulphuric acid at 50 C (122 F) for 2 minutes at 2 amp/dm^2 (19 amp/ft^2), with lead anodes.

Anode pickling "C". The procedure was the same as in "A", except that *after* step "5" the steel was pickled as anode in 96 percent sulphuric acid at room temperature. Lead cathodes were used, and a potential of 12 volts was applied until the high initial current dropped nearly to zero (usually in about 2 minutes). The plates were then rinsed quickly in cold water.

[3] The quoted numbers, capital letters, and sub-numerals used to identify the specimens, solutions, and conditions are the same as those employed in preliminary reports, and have been retained (with some omissions) for convenience of reference.

3. CONDITIONS USED IN PLATING

All the chemicals and anodes used in the plating were analyzed and found to be of good commercial quality. The solutions were analyzed at intervals and were adjusted to within about 2 percent of their nominal compositions.

(a) NICKEL PLATING

Rolled nickel anodes containing over 99 percent of nickel were used. The conditions of operation are summarized in table 1. The pH values there given were determined with a quinhydrone electrode, and are equivalent to "colorimetric corrected values", that is they are about 0.5 pH below the uncorrected colorimetric results.[4]

TABLE 1.—*Conditions in nickel plating*

Method[1]	Composition of solution												pH	Temperature		Current density		Variation
	$NiSO_4.7H_2O$			$NiCl_2.6H_2O$			Na_2SO_4			H_3BO_3								
	N	g/l	oz/gal	*N*	g/l	oz/gal	*N*	g/l	oz/gal	*M*	g/l	oz/gal		*C*	*F*	amp/dm²	amp/ft²	
E	1.4	200	27	0.4	45	6				0.5	30	4	5.3	35	95	2	19	Standard.
E_1	1.4	200	27	.4	45	6				.5	30	4	5.3	60	140	4	37	Temp. and c.d.
F	1.4	200	27	.4	45	6				.5	30	4	2.5	60	140	4	37	Low pH.
				NH_4Cl														
G	1.0	140	19	.25	15	2	2.0	140	19	.25	15	2	5.7	22	70	2	19	High SO_4.

[1] See footnote 3, p. 333.

(b) COPPER PLATING

Rolled copper anodes were used. The conditions employed in the copper baths were as follows:

Cyanide copper solution "L"	Approx. *N*	g/l	oz/gal
Copper cyanide, CuCN	0.25	22.5	3
Total sodium cyanide, NaCN	.65	34	4.5
Free sodium cyanide, NaCN	.15	7.5	1
Sodium carbonate, Na_2CO_3	.30	15	2
Temperature=50 C (122 F). Current density=1.5 amp/dm² (14 amp/ft²).			

[4] W. Blum and N. Bekkedahl, Trans. Am. Electrochem., Soc. 56,291(1929).

Acid copper solution "M"	*N*	g/l	oz/gal
Copper sulphate, $CuSO_45H_2O$	2	250	33
Sulphuric acid, H_2SO_4	1.5	75	10
Temperature=35 C (95 F).			
Current density=2.5 amp/dm² (23 amp/ft²).			

(c) CHROMIUM PLATING

An alloy of lead with 6 percent of antimony was used for the anodes. The different baths and conditions of operation are summarized in table 2.

TABLE 2.—*Conditions in chromium plating*

Method [1]	Composition of solution							Temperature		Current density		Variation
	CrO_3			H_2SO_4			Ratio $\frac{g\ CrO_3}{g\ SO_4}$					
	M	g/l	oz/gal	*N*	g/l	oz/gal		*C*	*F*	amp/dm²	amp/ft²	
I	2.5	250	33	0.05	2.5	0.33	100	45	113	16	150	Standard.
I_1	2.5	250	33	.05	2.5	.33	100	35	95	8	75	Temp. c.d.
I_2	2.5	250	33	.05	2.5	.33	100	55	131	27	250	Do.
I_3	2.5	250	33	.05	2.5	.33	100	65	149	38	350	Do.
I_4	2.5	250	33	.05	2.5	.33	100	45	113	8	75	C.d.
J	2.5	250	33	.025	1.25	.17	200	45	113	16	150	SO_4.
K	4.0	400	53	.08	4	.53	100	45	113	16	150	CrO_3.
K_1	4.0	400	53	.08	4	.53	100	55	131	27	250	Temp. c.d.
K_2	4.0	400	53	.08	4	.53	100	65	149	50	470	Do.

[1] See footnote 3, p. 333.

(d) ZINC PLATING (as an intermediate layer)

Cast zinc anodes were used in the following solution:

Cyanide zinc bath "N"	*N*	g/l	oz/gal
Zinc cyanide, $Zn(CN)_2$	1.0	60	8
Sodium cyanide, NaCN	0.5	23	3
Sodium hydroxide, NaOH	1.3	53	7
Temperature=22 C (70 F).			
Current density=2 amp/dm² (19 amp/ft²).			

(e) CADIUM PLATING (as an intermediate layer)

Cast cadmium anodes were used in the following solutions:

Cadmium bath (with gulac) "S"	*N*	g/l	oz/gal
Cadmium oxide, CdO	0.7	45	6
Sodium cyanide, NaCN	2.5	120	16
Gulac [1]		12	1.6
Temperature=22 C (70 F).			
Current density=2 amp/dm² (19 amp/ft²).			

[1] A by-product of the sulphite pulp industry.

Cadmium bath (with gulac and nickel) "T". The solution was the same as "S", with the addition of 1 g/l (0.13 oz/gal) of nickel sulphate, $NiSO_4.7H_2O$. The same temperature and current density were used.

4. BUFFING

Most of the nickel deposits were buffed, including those to be chromium plated. Allowance was made for the average loss in buffing similar specimens (usually from 10 to 20 percent), so that the final thicknesses were approximately those listed in tables 3 and 4. The chromium deposits were not buffed.

5. SCHEDULE OF DEPOSITS

The composition, thickness, and conditions used in depositing each coating are summarized in tables 3 and 4.

III. EXPOSURE TESTS

1. CONDITIONS OF EXPOSURE

(a) LOCATIONS

Five specimens of each set were exposed in the spring of 1932 in the following locations. In all except Washington and New York they were in enclosures used by the American Society for Testing Materials for other tests. In all places they were protected against unauthorized access.

At Key West (K.W.) Florida, at the United States naval station, they were frequently subjected to spray from the ocean. This represents a tropical marine exposure.

TABLE 3.—*Preparation of specimens with nickel finish*

[All thicknesses in inches, *=buffed]

Set no.	Cleaning[1]	Preliminary plating			Nickel plating		Variation
		Metal	Method[2]	Thickness	Method[3]	Thickness	
1	A				E	*0.001	Standard.
2	B				E	*.001	Cathode pickle.
3	C				E	*.001	Anode pickle.
4	A				E-1	*.001	High temp., high pH.
5	A				E	*.0005	Half thickness.
6	A				E	*.002	Double thickness.
7	A				F	*.001	Low pH.
9	A	Cu	L	0.0005	E	*.0005	Cu(CN), Ni.
10	A	Cu	L	*.0005	E	*.0005	Cu*(CN), Ni.
11	A	Cu Cu	L M	.0001 .0004	E	*.0005	Cu(CN), Cu(acid), Ni.
12	A	Cu Cu	L M	.0001 *.0004	E	*.0005	Cu (CN), Cu* (acid), Ni.
13	A	Cu	M	.0003	E	.0002 *.0005	Ni, Cu(acid), Ni.
14	A	Cu	L	.0003	E	.0002 *.0005	Ni, Cu(CN), Ni.
15	A	Cu	M	.00015	E	.0001 *.00025	Set 13, half thickness.
16	A	Cu	M	.0006	E	.0004 *.001	Set 13, double thickness.
17	A	Cu	M	.0003	F-1	.0002 *.0005	Set 13, with Ni at low pH.
18	A	Cu	M	.0003	E	.0002 *.0005	Set 13, heated 30 min to 200 C
19	A	Cu	M	.0003	F-1	.0002 *.0005	Low pH and heated 30 min to 200 C.
21	A	Zn	N	.0005	G	*.0005	Zn, Ni.
23	A	Cd	T	.0005	G	*.0005	Cd, Ni.
24	A	Zn Cu	N L	.0002 .0003	E	*.0005	Zn, Cu, Ni.
25	A	Cd Cu	T L	.0002 .0003	E	*.0005	Cd, Cu, Ni.
51	A				E	.001	Standard, not.*
52	A				E	*.00025	Standard, ¼ thick.
53	A	Cu	M	.00008	E	.00005 .00013	Set 13, ¼ thick.

[1] See p. 333. [2] See p. 334. [3] See table 1, p. 334.

TABLE 4.—*Preparation of specimens with chromium finish*

[All thicknesses in inches. *=buffed; **=heated after chromium plating]

1. ORIGINAL SETS

Set number	Cleaning	Preliminary plating as in set no.[1]	Chromium plating		Variation
			Method[2]	Thickness	
101	A	1	I	0.00002	Ni-standard.
102	B	2	I	.00002	Ni-cathode pickle.
103	C	3	I	.00002	Ni-anode pickle.
104	A	4	I	.00002	Ni-high temp., high pH.
105	A	5	I	.00002	Ni, 0.0005.
106	A	6	I	.00002	Ni, 0.002.
107	A	7	I	.00002	Ni, low pH.
109	A	9	I	.00002	Cu (CN), Ni.
110	A	10	I	.00002	Cu* (CN), Ni.
111	A	11	I	.00002	Cu (CN), Cu (acid), Ni.
112	A	12	I	.00002	Cu (CN), Cu * (acid), Ni.
113	A	13	I	.00002	Ni, Cu (acid), Ni.
114	A	14	I	.00002	Ni, Cu (CN), Ni.
115	A	15	I	.00002	Ni, Cu (acid), Ni (0.0005).
116	A	16	I	.00002	Ni, Cu, Ni (0.002).
117	A	17	I	.00002	Ni, Cu, Ni, low pH.
118**	A	18	I	.00002	Ni, Cu, Ni, heated.
119**	A	19	I	.00002	Ni, Cu, Ni, low pH, heated.
121	A	21	I	.00002	Zn, Ni.
123	A	23	I	.00002	Cd, Ni.
124	A	24	I	.00002	Zn, Cu, Ni.
125	A	25	I	.00002	Cd, Cu, Ni.
126	A	13	I	.00001	Thickness of Cr.
127	A	13	I	.00003	Do.
128	A	13	I	.00005	Do.
129	A	13	I-1	.00002	Cr at 35 C.
130	A	13	I-2	.00002	Cr at 55 C.
131	A	13	I-3	.00002	Cr at 65 C.
132	A	13	J	.00002	CrO_3/SO_4 ratio=200.
133	A	13	K	.00002	400 g/l CrO_3.
134	A	none	I	.0002	Direct Cr thick.
135	A	none	I-2	.0002	Cr ar 55 C.
136	A	none	I-3	.0002	Cr at 65 C.
137	A	Cd *, S, 0.0005	I-1	*.00002	Cd, Cr.
138	A	Zn*, N, 0.0005	I-1	*.00002	Zn, Cr.
152	A	52	I	.00002	Ni (0.00025).
153	A	53	I	.00002	Ni, Cu, Ni (0.00025).
154	A	13	I	.0001	Thickness of Cr.
155	A	13	K-1	.00002	400 g/l CrO_3, 55 C.
156	A	13	K-2	.00002	400 g/l CrO_3, 65 C.

2. SUPPLEMENTAL SETS

157	A	5	I	0.00001	Thickness of Cr.
158	A	5	I	.00003	Do.
159	A	5	I	.00005	Do.
160	A	15	I	.00001	Do.
161	A	15	I	.00003	Do.
162	A	15	I	.00005	Do.
163	A	5	J	.00002	Sulphate ratio.
164	A	15	J	.00002	Do.
165	A	5	I-4	.00002	Current density.
166	A	15	I-4	.00002	Do.
167	A	5	I-1	.00002	Temperature.
168	A	15	I-1	.00002	Do.
169	A	1	I	.00001	Thickness of Cr.
170	A	1	I	.00003	Do.

[1] See table 3.
[2] See p. 334.

At New York (N.Y.), on the sixth story roof of the Bell Laboratories, considerable smoke from adjacent buildings and vessels produced an industrial urban atmosphere.

At Pittsburgh (P.), Pa., on Brunot's Island in the Ohio River, there was much smoke and fog, representing a severe industrial exposure.

At Sandy Hook (S.H.), N.J., on the Fort Hancock Reservation they were close to the ocean. In addition to the salt spray, representing a northern marine exposure, there was probably a slight industrial contamination from nearby vessels and locomotives and from cities surrounding New York harbor.

At State College (S.C.), Pa., they were in a field far removed from any buildings. This represents an uncontaminated rural atmosphere.

At Washington (W.), D.C., on the roof of a one-story building at the National Bureau of Standards, they were subject to only small concentrations of smoke from the heating plant and from nearby dwellings. This is a typical suburban atmosphere.

(b) RACKS

The specimens were supported on galvanized steel racks by means of porcelain insulators, which prevented contact with any metals. The racks were attached to supports so that the specimens were inclined 30 degrees from horizontal and faced south. The installation in Washington is illustrated in figure 1.

2. INSPECTION

At specified intervals, at first of a few weeks and later of a few months, the specimens were examined by members of the joint inspection committee and other interested persons. The average number of persons at each inspection was three. Over 100 inspections were made in the 6 locations in about 2 years.

(a) METHOD OF RATING

The approximate proportion of the surface rusted was expressed by the scale of ratings shown in table 5.

TABLE 5.—*Rating of specimens*

Surface rusted	Rating	Corresponding percentage score	Surface unrusted
Percent			*Percent*
0	5	100	100
0 to 5	4	80	95 to 100
5 to 10	3	60	90 to 95
10 to 20	2	40	80 to 90
20 to 50	1	20	50 to 80
50 to 100	0	0	0 to 50

Rust within 0.25 in. of an edge was disregarded, as on some specimens the coatings near the edge were reduced in thickness by the buffing. Each inspector assigned a numerical rating to each specimen, and the average of the ratings of all the inspectors for each set of specimens constituted the recorded rating for that set, location and inspection date. The mean of this and the rating at the preceding inspection, that is, the average rating for that period, was multiplied by the number of weeks intervening to obtain the "score" for the period. The total score for the entire period was compared with a perfect score for the same period to obtain the "percentage score." If, for example, the ratings for a set at intervals of 4 weeks were 4

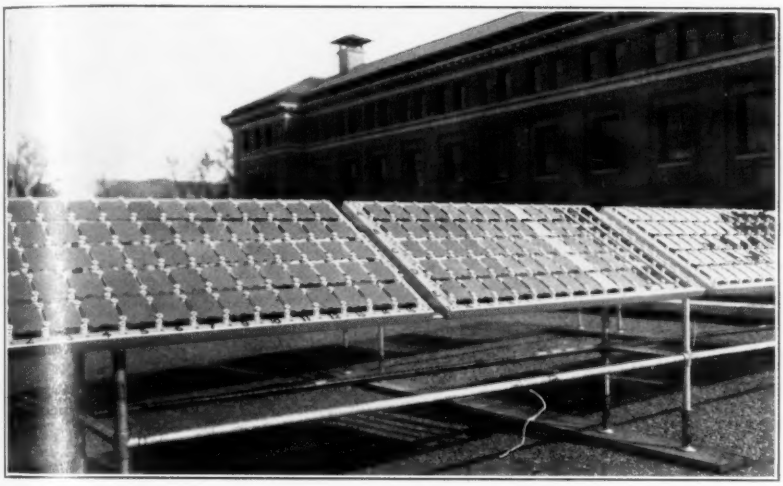

FIGURE 1.—*View of exposure tests at Washington, D.C.*

NOTE.—The dark areas on some specimens are the result of reflections and not of corrosion.

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and 3, respectively, the average rating for that period was 3.5, and the score was $3.5 \times 4 = 14$. If the total score for the 20 weeks previously elapsed was 76, the score for the entire 24 weeks was $76 + 14 = 90$, instead of the possible $24 \times 5 = 120$, and the percentage score was $\frac{90}{120} = 75$ percent.

The net result was to express the quality on a percentage basis, which, however, as shown in table 5, is not proportional to the percentage of unrusted surface. In other words, the quality score is not linear with respect to the proportion of rust, but is roughly logarithmic. This is an expression of the fact that a very small proportion of rust may indicate both in protection and appearance a relatively unsatisfactory coating. While this system appears to represent fairly the relative protective values of the coatings, it is important to note that a set with an average score of only 60 percent may have less than 10 percent of rusted area.

A detailed study of the data showed that when three or more experienced persons conducted successive inspections, the probable error of the average result for a set was about ± 0.2 unit on a scale of 5, corresponding to 4 percent. However, as the number and identity of the inspectors varied at different times and locations, it is doubtful whether differences of less than about 10 percent in the final scores are significant. No doubt the ratings would have been more consistent and more nearly comparable in different locations if all the inspections had been made by the same group, for example of three persons. This was not practicable.

(b) APPEARANCE

In addition to ratings based on rust, notations were made regarding the presence of other defects in the appearance, such as white or dark stains, blisters, cracks, and peeling. No attempt was made to assign numerical values to these defects, and it is difficult to decide upon the weight to be given them in the final evaluation of the data, which are discussed on p. 352.

3. SIGNIFICANCE OF EXPOSURE TESTS

(a) RELATION TO SERVICE

The most important question in the practical application of results of exposure tests is whether they represent fairly the conditions to which articles in service are actually subjected. This question cannot be answered exactly because the conditions under which plated articles are used are far more varied than are actual climatic conditions. Plated metals are subjected to three general classes of atmospheric exposure, (a) indoors, where the temperature and humidity do not vary greatly; (b) continuous outdoor exposure without cleaning, such as on pole-line hardware; and (c) intermittent outdoor exposure, which is usually accompanied by occasional cleaning operations, illustrated by the bright plating on automobiles. Of course, there are many other types of exposure that may cause corrosion, for example, exposure to soil, to washing materials, to specific chemicals, and to high temperatures. It is unsafe to apply to such corrosion the data obtained in simple atmospheric tests.

Without attempting to set an exact relation, it is probably fair to assume that any plated coatings that will furnish protection for a year or more outdoors in a noncorrosive atmosphere, such as at State College and Washington, will last almost indefinitely under normal household or office conditions. For class (b), for which zinc and cadmium are most commonly used, exposure tests that involve no cleaning during exposure represent actual conditions of service. For class (c), however, which is probably the most important use of plating, it is difficult to correlate the exposure tests with actual service. Most automobiles are washed frequently, and at the same time it is customary and desirable to rub the polished plated parts with grease or wax such as is applied to the body finish. These treatments undoubtedly prolong the protective value of the plating, (1) by removing the surface films which are likely to retain moisture and other corrosive constituents of the atmosphere, (2) by filling pores with grease, and (3) by reducing the tendency of the surface to be wet by water.

Any attempt to introduce these treatments into exposure tests would lead to complications that might obscure entirely the protective value of the metal coatings themselves. Serious consideration was given to the possibility of washing all the specimens at regular intervals. The objections which prevented the adoption of this course are as follows: (1) The physical task of bringing an ample supply of clean water would be very great, as many of the racks were in isolated spots, far removed from a supply of fresh water. (2) The time and labor required to clean over 500 specimens in each locality would be great. (3) It would be difficult to have the cleaning done uniformly at different times or in different locations, and to avoid variations in the technic of cleaning, such as the stiffness of the brush, the pressure applied, and the thoroughness of rinsing. (4) The cleaning would probably remove some of the rust, so that it would be necessary to rate the specimens either before cleaning on that day, or a definite short period such as one or two weeks after cleaning. This would increase the time and expense required for the inspections.

As the specimens were not cleaned during the first 18 months' exposure, the results represent only the relative and not the actual life of each coating when in service. In New York and Pittsburgh, removal of the dark films after 18 months had very little effect on the appearance of the specimens after a few weeks' subsequent exposure, because these specimens had already failed badly. In marine locations, where the rust was distinct, it was usually so thin during the early stages of failure that light rubbing would have almost completely restored the original appearance. It is probable that 1 year's exposure in any of the severe locations was equivalent to at least a few years of normal usage in the same climate.

It is difficult to define "failure" in terms of the rating scale here used, or of any other arbitrary scale. As a rating of 4 may represent very few rust spots, one of 3, that is, from 5 to 10 percent of rust, really represents the first significant failure. If a coating does not go below 3 in the first year in a severe location, it has a good protective value. Practically, this is equivalent to a score of about 70 percent, which may then be used as an index of failure. As stated above, this is equivalent to an unrusted area of at least 90 percent.

Since the main purpose was to determine the relative protective values of the various coatings, and especially to learn the effect of each

of the factors upon the protective value, it is believed that differences of 10 percent or more in the scores are probably significant, while differences as low as 5 percent are significant only if they are consistent in different locations.

Another factor that must be considered in the application of these results is the distribution of the coatings on the plated surfaces. This was more uniform on these flat plates than it can be made on irregularly shaped articles. In plating the latter, the better throwing power of a particular solution may be significant, even though a given thickness of the deposit has no better protective value.

(b) RELATION TO PLATING OF OTHER BASE METALS

In any effort to estimate the protective value of plating from this investigation, it should be noted that the results apply only to the use of steel as the base metal. It is hoped to extend this study to include other base metals such as copper, brass, zinc, and aluminum. With the aid of the information thereby obtained, it should be possible to decide what base metal and what kind and thickness of plating would prove most suitable and most economical for any given application.

IV. RESULTS AND DISCUSSION

In the following discussion, reference will be made chiefly to the extent of rust, and the appearance will be referred to only when it seems to modify seriously the conclusions based on rust. Before discussing the results obtained with different coatings, the reproducibility of the data warrants consideration.

1. REPRODUCIBILITY

In at least 80 percent of all inspections, the ratings for the 5 specimens of a set were identical, and less than 2 percent of the specimens were distinctly erratic. Such uniform coatings can be produced only under conditions where each variable is under close control.

The ability to reproduce the coatings in an independent operation was determined in supplemental exposures in the 4 severe locations of 10 sets, each consisting of 2 of the original specimens that had been carefully preserved and 3 new specimens plated about a year later. The average difference in the two parts of each set was only 4.4 percent, which is just about the reproducibility of the observations. In only 2 sets was this difference greater than 5 percent, the old specimens of no. 113 being 14 percent inferior and of no. 126 being 10 percent inferior to the new specimens. Except for these discrepancies, which are not great, it is evident that specimens can be duplicated by following the same procedures.

2. SEASONS

The conclusions may be affected by the reproducibility of the weather at any location. This may be judged from the 10 sets used in the original and the supplemental exposures in 4 locations, by comparing the results obtained in 1932 with those for a similar period in 1933. In New York and Sandy Hook the results for the 2 years were about the same. In Key West the average score was about 30 percent less in 1932 than in 1933. This corresponds to a much heavier

rainfall in Key West in 1932 in 7 out of the 8 months considered in this comparison. The 20 percent more severe corrosion in Pittsburgh in 1932 than in 1933 probably corresponds to a difference in industrial activity there, for which no exact figures are available.

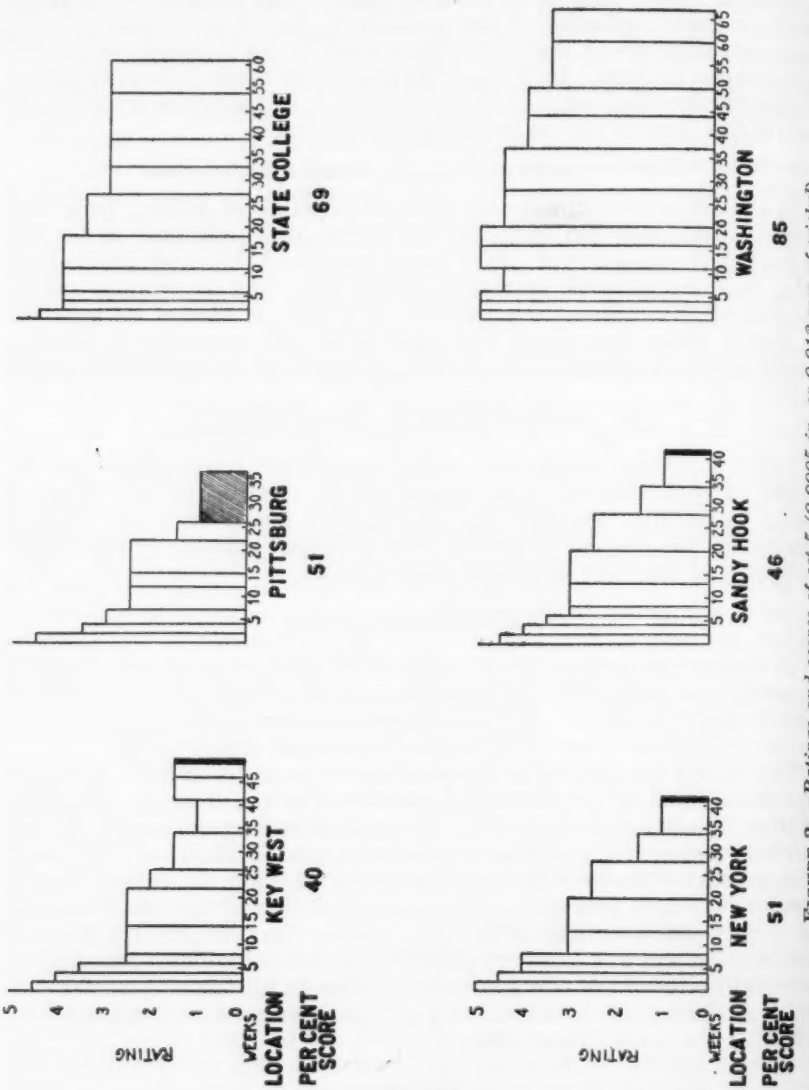

FIGURE 2.—*Ratings and scores of set 5 (0.0005 in. or 0.013 mm of nickel).*

3. LOCATION

The results for different locations are summarized in table 6 and illustrated in figure 2. In this figure the behavior of set 5 (0.0005 in. of nickel) in the 6 locations is shown in a way that also illustrates the method of computing the scores. Each narrow rectangle represents the product of an average rating and a number of weeks. The total area under the horizontal lines represents the total score, and its ratio

to a rectangle with a height of 5, is the percentage score. The fact that ratings at one inspection were occasionally superior to those at a preceding inspection is illustrated in the diagrams for Key West and Washington. Such discrepancies may arise from personal errors in rating, or from an actual improvement in appearance caused by removal of rust by heavy rains.

TABLE 6.—*Effect of location on protective value of coatings*

[18 months exposure]

Nickel and chromium finishes. Total thickness—0.001 in. (0.025 mm)

Number of sets	Coating	Percent scores					
		K.W.	N.Y.	P.	S.H.	S.C.	W.
5	Ni	71	65	36	63	86	86
9	Cu and Ni	29	76	23	53	88	93
5	Ni, Cr	58	72	23	51	98	94
9	Cu and Ni, Cr	40	68	20	46	97	95
Average		50	70	26	54	92	91

In the 2 marine locations the averages are very close and in each place the rust was distinct and easily rated. The detrimental effect of copper in the absence of chromium (to be discussed later) was more pronounced at Key West than at Sandy Hook. Another difference, not shown in table 6, is that more small blisters developed at Sandy Hook. This fact, and the more rapid failure of both zinc and cadmium coatings in Sandy Hook than in Key West (to be reported in a later paper), indicate that there is some industrial contamination at Sandy Hook in addition to the marine atmosphere.

At New York and Pittsburgh the behavior was more similar than is indicated by the numerical values, though the failure was much more rapid in Pittsburgh, especially during the first 6 months (from April to October 1932) when there was industrial smoke in Pittsburgh but very little smoke in New York until heating was required in buildings. In these locations both buffed and unbuffed specimens became nearly black, so that it was difficult to determine whether rust was present. Microchemical examination showed that these black films contained very little carbon, but consisted largely of black magnetic oxide of iron, Fe_3O_4. The following tentative explanation for its formation is suggested. In each of these locations there was an appreciable concentration of sulphur dioxide (and possibly of sulphuric acid) in the atmosphere. This penetrated any pores and caused attack of the steel, to form ferrous sulphite, which was identified as a light green layer next to the steel. Further oxidation produced the more soluble ferrous sulphate, which exuded, spread over the surface, and, in the presence of sulphur dioxide was only partly oxidized, to form the black oxide. In addition, the sulphur compounds rapidly etched the nickel surfaces and no doubt increased the number and size of the pores. There was much less etching of the chromium-plated surfaces.

It is apparent, therefore, that these black films were just as much evidence of corrosion of base metal as was the appearance of red rust. However, as it was more difficult to define and evaluate the

extent of the dark films, the ratings in New York and Pittsburgh were less concordant than elsewhere, and the percentage scores are less reliable.

At State College and Washington there was very little rust on any coatings that were 0.001 in. or more in thickness, although the very thin coatings failed rapidly there and elsewhere. The slight extent of rust on thick coatings at State College and Washington, and the

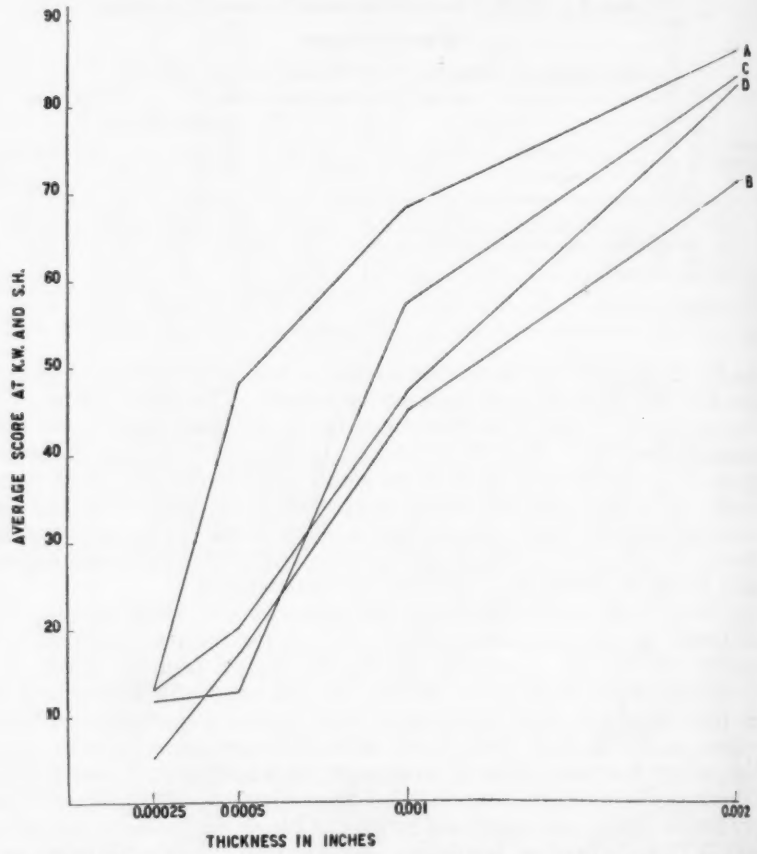

FIGURE 3.—*Effect of thickness on protective value during first 15 months exposure in marine locations.*

A, nickel; B, nickel, copper, nickel; C, nickel+0.00002 in. (0.0005 mm) of chromium; D, nickel, copper, nickel+0.00002 in. (0.0005 mm) of chromium. Plotted values for 0.001 in. are averages of 5 or more sets.

difficulty of rating the specimens at New York and Pittsburgh, make the results at Key West and Sandy Hook more conclusive than the others. Attention will be called, however, to those cases in which the results elsewhere appear to contradict those of marine exposure.

4. PROTECTION AGAINST CORROSION

The following conclusions are based on over 100,000 individual ratings of specimens. The data were assembled and summarized into extensive tables showing the effects of the different variables.

These tables are too long to warrant complete publication, but they were available to the joint committee and to about 25 other interested persons, who agreed to the following conclusions in all essential respects. Sufficient data and figures will be included to show the magnitudes involved. The effects of each important variable will be discussed separately. Unless otherwise specified, the conclusions are based on the original exposures for 18 months, from March 1932 to October 1933. When mention is made of the supplemental tests, the period of 14 months from January 1933 to March 1934 is referred to.

(a) NICKEL COATINGS

(1) *Thickness.*—The total thickness of nickel (or copper and nickel) coatings is the most important factor in their protective value, regardless of whether or not chromium is also applied. As shown in table 7 and figure 3, coatings with a thickness of only 0.00025 in. (0.006 mm) are practically worthless for outdoor exposure in any location, and those with a thickness of 0.0005 in. (0.013 mm) are valuable only in mild locations, S.C. and W. Except in Pittsburgh, fair protection was obtained with 0.001 in. (0.025 mm) and almost perfect protection with 0.002 in. (0.05 mm) of nickel. It is evident that the most practical way of increasing the protective value of nickel deposits is to increase their thickness.

TABLE 7.—*Effect of thickness of nickel and conditions of deposition on protective value of coatings*

Nickel finish. 18 months' exposure. Percent scores

Set number	Procedure	Thickness	K.W.	N.Y.	P.	S.H.	S.C.	W.	Average (6)	Marine, average K.W., S.H.	Industry, average N.Y., P.	Suburban, average S.C., W.
		In.										
52	Standard	0.00025	10	17	8	10	31	35	19[a]	10	13	33
5	do	.0005	25	30	20	27	70	82	42	26	25	76
1	do	.001	67	67	36	62	87	86	68	65	52	87
2	Cathode, pickling	.001	54	67	36	64	91	87	68	59	52	89
3	Anode, pickling	.001	76	66	36	68	89	87	70	72	51	88
4	High temperature, high pH	.001	79	62	36	61	86	87	69	70	49	87
7	High temperature, low pH	.001	54	61	34	62	77	83	62	58	48	80
51	Standard, not buffed	.001	31	61	37	56	87	91	61	44	49	89
	Average (with 0.001)	.001	60	64	36	62	86	87	66	61	50	87
6	Standard	.002	79	86	52	79	96	94	81	79	69	95

(2) *Conditions of deposition.*—The data in table 7 for sets with 0.001 in. (0.025 mm) of nickel, show that the maximum variation from the average of the 6 sets in 6 locations was only 5 percent. It is evident that none of the conditions used in the preparation of nickel plating had any marked effect on the protective value. That the apparent slight inferiority of the low pH nickel deposits "7", observed especially at Key West, was probably not significant, is shown by the fact that when the same nickel deposits were plated with 0.00002 in. (0.0005 mm) of chromium, the specimens plated at the low pH were correspondingly better than the average. The unbuffed nickel

deposit "51" behaved about the same as the average buffed deposit, except in Key West, where it was decidedly inferior.

(b) EFFECT OF COPPER LAYERS IN NICKEL DEPOSITS

Copper is sometimes applied to the steel as an initial layer, in which case cyanide solutions are used, and sometimes as an intermediate layer between two nickel deposits. In the latter application, either cyanide or acid copper solutions may be employed. In these tests, four sets consisting of nickel, acid copper and nickel, were prepared with different total thicknesses, and nine sets with a total thickness of 0.001 in. (0.025 mm) were prepared with different combinations of copper and nickel. (See table 3.) The results in table 8 and in curves *B* and *D* of figure 3 represent a comparison of these coatings with pure nickel deposits of the same total thickness, that is, they show the effects of substituting copper for part of the nickel. The use of the average of 9 sets is justified because the maximum deviation in these sets with the same thickness was only 10 percent; in other words, about the same protection was obtained with copper deposits of a given thickness from acid and from cyanide solutions.

TABLE 8.—*Effect of a layer of copper on the protective value of coatings*

Percent variation in scores from those of pure nickel deposits of same total thickness

Thickness	K.W.	N.Y.	P.	S.H.	S.C.	W.	Average (6)	Marine, average, K.W., S.H.	Industrial, average N.Y., P.	Suburban, average S.C., W.
In.										
0.00025	−7	+2	−2	−5	−18	−18	−8	−6	0	−18
0.0005	−18	+15	−3	−8	+5	+4	0	−13	+6	+5
0.001 (avg. of 9)	−42	+11	−13	−10	+2	+6	−8	−25	0	+4
0.002	−19	+8	−17	−1	+4	+4	−3	−10	−4	+4
Average	−21	+9	−9	−6	−2	−1	−5	−14	0	1−

It is apparent from table 8 that in very thin coatings the presence of copper is practically always detrimental. This harmful effect of copper persists in thicker deposits in the two marine locations and in Pittsburgh, but not in New York, State College, or Washington. If this effect of copper is caused by electrolytic acceleration of the corrosion of any steel exposed in pores, we would expect it to be more pronounced when an electrolyte is present, such as the salt water in marine locations or the sulphurous acid in a severe industrial atmosphere.

In supplemental exposures, the copper was also detrimental in the two marine locations, but beneficial in both New York and Pittsburgh. The discrepancy in the last place is consistent with the fact that in 1933 the general corrosion was less severe in Pittsburgh than in 1932. The beneficial effect of copper in thick deposits in urban locations is consistent with the results previously obtained at the same site in Washington.[6] It illustrates the danger of drawing general conclusions on corrosion from results in a single location.

[6] C.T. Thomas and W. Blum, Trans. Am. Electrochem. Soc., **48**,69(1925), and **52**,277(1927).

In all cases, those deposits in which the copper layer was buffed before the application of the final nickel layer were found to be slightly superior to those with unbuffed copper. It is probable that this advantage of buffing the copper would have been more noticeable if the steel had had more defects in the surface than did the steel used in this study.

As indicated in figure 3 the detrimental effect of copper in thick deposits in marine locations is nearly overcome by the application of chromium, or, more strictly speaking, the chromium has a somewhat detrimental effect on the pure nickel deposits but not on those containing copper. No explanation is offered for this curious counteracting of effects. The net result is that copper is not objectionable in thick deposits if chromium is applied.

(c) EFFECTS OF CHROMIUM

(1) *Chromium directly on steel.*—Three sets (134, 135, 136) were plated directly with 0.0002 in. (0.005 mm) of chromium, at temperatures respectively of 45, 55, and 65 C. In all locations they rusted badly within a few months and were generally inferior to specimens with 0.00025 in. (0.006 mm) of nickel or of copper and nickel. This result is consistent with the well-known porosity of chromium deposits. Although those produced at 65 C had a distinctly better protective value than those at 45 or 55 C, they were too poor to warrant consideration for outdoor exposure.

(2). *Effect of 0.00002 in. (0.0005 mm) over nickel.*—As the average commercial thickness of chromium for exposed metal parts is now about 0.00002 in., this thickness was applied (under "standard" conditions) to a large number of plates with deposits of nickel or of copper and nickel. The results show what effects may be expected under average conditions.

The addition of this thickness of chromium to nickel deposits had much the same effect as an intermediate layer of copper, that is it reduced by about 10 percent the protective value of the coatings in marine (K.W. and S.H.) and severe industrial (P.) atmospheres, but correspondingly improved the protection in the other three locations. In all locations, however, the chromium preserved the appearance, especially the luster, of those parts of the surface that were not rusted. It is evident therefore that in severe exposures the protection furnished by composite coatings is determined principally by the thickness and quality of the nickel deposits. This confirms the frequent statement that "the nickel protects the steel from rusting, and the chromium protects the nickel from tarnishing."

The application of this thickness of chromium over composite coatings of copper and nickel improved their protective value, especially at Key West. As shown in figure 3, when chromium is applied as the final finish over thick deposits, there is very little difference in the protection afforded by the pure nickel deposits and by those containing a copper layer. This result apparently justifies the use of a copper layer when it is otherwise expedient [7] to employ it.

[7] Among the practical reasons for using a copper layer are (a) the greater ease of covering slight defects in the steel, especially if the copper is buffed, (b) the more ready detection of copper than of steel if the final nickel layer is accidentally cut through in the final buffing operation, and (c) the lower cost of copper.

(3) *Variations in thickness.*—It was shown by E. M. Baker and A. M. Rente [8] and confirmed by others [9] that as the thickness of chromium deposits is increased, their porosity decreases to a minimum and then increases. The latter effect is caused principally by the development of fine cracks in the chromium deposits. On this basis it has been predicted that there is a certain optimum thickness of chromium (usually about 0.00002 to 0.00003 in.), and that thinner or thicker deposits furnish less protection. It was therefore important to determine whether these predictions would be confirmed in actual atmospheric tests.

In the first exposures, only one series of specimens was used to determine the effect of the thickness of chromium, which was applied

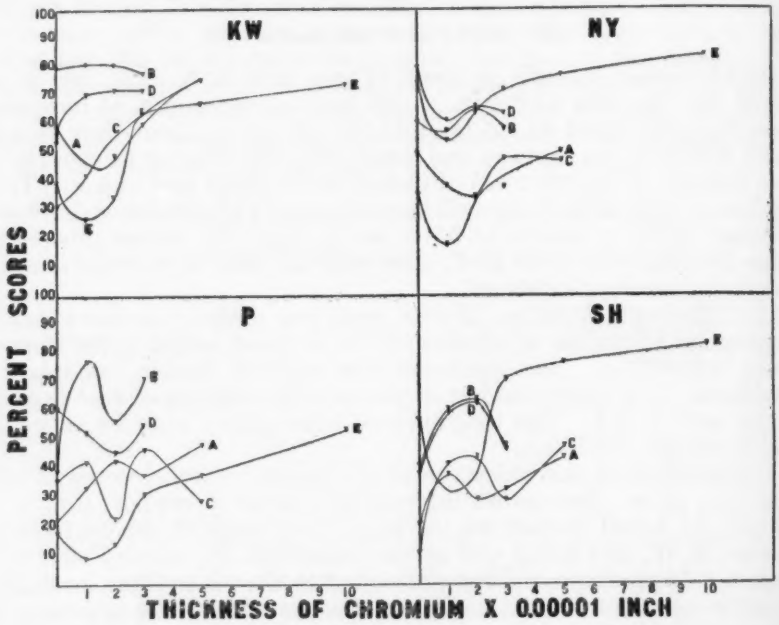

FIGURE 4.—*Effect of thickness of chromium on protective value.*

Chromium applied over

Coating	Thickness	Exposure	Months
	In.		
A—nickel	0.0005	Supplemental	14
B—nickel	.001	do	14
C—nickel, copper, nickel	.0005	do	14
D—nickel, copper, nickel	.001	do	14
E—nickel, copper, nickel	.001	Original	18

over nickel, copper, nickel coatings with a total thickness of 0.001 in. The results, shown in curves E in figure 4 were consistent in all locations. They showed a decided detrimental effect of a very thin chromium coating (0.00001 in.) followed by a marked and continuous increase in protective value as the thickness of the chromium was

[8] E. M. Baker and A. M. Rente, Trans. Am. Electrochem. Soc., **54**, 337 (1928).
[9] W. Blum, W. P. Barrows, and A. Brenner, BS J. Research **7**, 697, (1931); RP 368.

increased. As the latter effect was unexpected, four new series were included in supplemental tests, which yielded the results shown in curves A, B, C, and D, of figure 4.

While there is considerable variety in the shapes and positions of these curves, it is evident that there is no consistent detrimental effect of 0.00001 in. of chromium. Between 0 and 0.00003 in. of chromium there is almost always a minimum protective value. The positions of these minima differ, so that it is practically impossible to select a definite thickness of chromium that gives either minimum or maximum protection. Perhaps the most significant conclusion is that from 0.00001 to 0.00003 in. of chromium is a critical range, in which a slight variation in thickness (or perhaps in the conditions of deposition) may either increase or decrease the protective value.

The practical significance of this conclusion is increased by the fact that on irregularly shaped articles that are plated with an average of, for example, 0.00002 in. of chromium, some portions of the surface may have either 0.00001 or 0.00003 in. of chromium. Even if it were possible to define closely an optimum thickness of chromium, it would be practically impossible to apply it uniformly to many articles. It is therefore fortunate that the total protective value of the coatings is determined much more by the thickness of nickel (or of copper plus nickel) than by that of the chromium. This is shown by the fact that in figure 4, curves B and D (for 0.001 in. undercoat) are above curves A and C (for 0.0005 in. undercoat).

The greater protective value in most locations of the relatively thick chromium coatings (0.00005 and 0.0001 in.) is surprising in view of the previously reported greater porosity of such coatings, which was confirmed by tests with the copper-deposition method on specimens similar to those used in the exposure tests. The value of thick chromium deposits is illustrated by the fact that, after 2 years' exposure, set 154 (consisting of 0.001 in. of Ni, Cu, Ni and 0.0001 in. of chromium) is superior to any other sets with this same thickness of nickel or of copper plus nickel, and is about equal to sets 106 and 116, which have 0.002-in. undercoats and 0.00002 in. of chromium. No entirely satisfactory explanation is known for the greater protective value of these thick chromium coatings, that undoubtedly contain many cracks. It is tentatively suggested that it may be caused by the greater tendency for the initial products of corrosion to seal the narrow cracks in a thick coating than in a thin coating. From a practical standpoint the result suggests the use of relatively thick chromium deposits for very severe conditions, and especially in an industrial atmosphere containing sulphur dioxide, which rapidly attacks nickel but not chromium.

(4) *Conditions of deposition.*—In chromium deposition both the temperature and current density must be controlled to yield bright deposits. In preparing specimens for the original exposures, the temperature of deposition was varied from 35 to 65 C (95 to 149 F) and the current densities (see table 2) were selected to yield bright deposits with about 12 percent cathode efficiency. It was found that the deposits produced at 35 C were consistently about 15 percent superior to those produced at 45, 55, or 65 C. The latter three sets were about equal. This small but definite improvement contradicts the results of porosity tests which showed that the deposits made at

35 C were more porous than those made at higher temperatures. Changes in temperature at a constant current density, or in current density at a constant temperature (within the bright plating range) showed very little effect on the protective values of the coatings.

Changes in the concentration of chromic acid from 250 to 400 g/l (33 to 53 oz/gal) had no definite effect on the value of the coatings. A decrease in sulphate content, that is an increase in the ratio, $\frac{g\ CrO_3}{g\ SO_4}$, from 100 to 200 (at 45 C and 16 amp/dm^2 or 150 amp/ft^2), made a consistent improvement of about 20 percent in the scores, both in the original and the supplemental tests. This beneficial effect of a high "sulphate ratio" corresponds with the lower porosity of such deposits, previously reported from this Bureau [10] and also confirmed by tests of these deposits.

Heating the chromium plated specimens to 200 C (392 F) for 30 minutes had no effect on their protective value in the atmosphere, though R. J. Wirshing [11] reported that it improved their resistance to calcium chloride.

(d) EFFECTS OF INTERMEDIATE ZINC OR CADMIUM LAYERS

As both zinc and cadmium coatings furnish electrolytic protection against corrosion of steel but tend to tarnish quickly in the atmosphere, it has often been suggested that such metals should be used as initial layers to be followed by coatings of nickel or chromium. It was early shown,[12] however, that the application of a more noble metal, such as nickel, over zinc reduced the protective value of the latter, as the corrosion of any zinc exposed through pores in the nickel was thereby accelerated.

The results of the exposure tests of these coatings are given in detail in table 9. A comparison of the scores for sets 1 and 21, shows that in all localities the substitution of zinc for part of the nickel reduced the protective value below that of either metal alone. This effect was most marked for the mild exposures (in S.C. and W.).

TABLE 9.—*Effects of zinc and cadmium under nickel and chromium*

1. NICKEL FINISH—18 months exposure—Total thickness = 0.001 in.

Set number.	Undercoat [1]	K.W.	N.Y.	P.	S.H.	S.C.	W.	Average (6)	Marine average K.W. S.H.	Industrial average N.Y. P.	Suburban average S.C. W.
1	(Ni 0.001)	67	67	36	62	87	86	68	65	52	87
21	Zn 0.0005	59	48	31	49	60	59	51	54	40	60
23	Cd 0.0005	48	63	36	64	90	88	65	56	50	89
24	Zn 0.0002 Cu 0.0003	67	74	40	86	93	92	76	77	57	93
25	Cd 0.0002 Cu 0.0003	42	75	46	78	96	91	71	60	61	94

[1] Followed by 0.0005 in. of nickel except in sets 137 and 138.

[10] See footnote 9.
[11] Trans. Am. Electrochem. Soc. **58**, 89 (1930).
[12] O. P. Watts and P. L. Derverter, Trans. Am. Electrochem. Soc. 30, **145** (1916).

TABLE 9.—*Effects of zinc and cadmium under nickel and chromium*—Continued

II. CHROMIUM FINISH (0.00002 Cr)—Total thickness 0.001 in.

(1) Over Nickel

Set number	Undercoat	K.W.	N.Y.	P.	S.H.	S.C.	W.	Average (6)	Marine average K.W. S.H.	Industrial average N.Y. P.	Suburban average S.C. W.
101	(Ni 0.001)	54	69	23	47	100	99	65	51	46	100
121	Zn 0.0005	81	47	20	65	85	80	63	73	34	83
123	Cd 0.0005	71	63	22	79	97	93	71	75	43	95
124	Zn 0.0002 / Cu 0.0003	75	60	24	81	87	97	71	78	42	92
125	Cd 0.0002 / Cu 0.0003	63	59	29	77	90	95	70	70	44	97

(2) Over Zinc or Cadmium (No Nickel)

137	Cd 0.0005	38	67	64	78	93	87	71	58	66	90
138	Zn 0.0005	38	79	77	88	95	79	76	63	78	87

During the first few months of exposure, white spots appeared over the surface, and a few months later decided rust appeared. It appears therefore that the nickel accelerated not only the corrosion of exposed zinc, but also of iron that was exposed when the zinc was penetrated, even though some zinc was still adjacent to the iron. The specimens with 0.0005 in. each of zinc and nickel rusted much more rapidly than those in the parallel tests with 0.0005 in. of zinc and no nickel.

When chromium was applied (121) over the zinc-nickel coatings, the results were less consistent. At Pittsburgh, State College, and Washington, the effect of the zinc layer was detrimental while at Key West and Sandy Hook it was beneficial. It is difficult to explain why the chromium coating (which had very little if any effect on the porosity of the coatings) should counteract the detrimental effect of zinc in marine locations. The results in table 9 show that the introduction of a cadmium layer under the nickel had very little effect on the protective value. When chromium was also present, the cadmium was beneficial in marine locations.

The difference in the behavior of zinc and cadmium as undercoats is consistent with the fact that the standard potential of cadmium is closer to that of nickel than is the potential of zinc, and hence the corrosion of the cadmium is less accelerated by contact with nickel.

The application of a layer of copper between the zinc and nickel overcame the detrimental effect of the zinc. No explanation is offered for the fact that one noble metal (copper) counteracted the accelerating effect of another noble metal (nickel). The copper had no marked effect on the protective value of composite coatings containing cadmium.

Coatings with a layer of chromium over cadmium, "137", or over zinc, "138", became dull after a few months' exposure. Later, numerous very fine rust spots appeared. While the scores based on the percentage of rust are relatively high, these composite coatings are not desirable where appearance is an important consideration.

5. APPEARANCE

As previously noted, a record was kept of all significant changes in appearance. It was impracticable to devise any numerical system of rating to cover all the defects that might appear, such as light or dark stains, large or small blisters, cracking and peeling. It is difficult to decide how much weight to attach to appearance apart from corrosion, even though it is one of the most important factors in the choice and value of plated coatings. A coating which furnishes very little protection against corrosion of the steel is practically useless whether other defects develop or not. The consideration of appearance may therefore be confined principally to those coatings which furnish at least fair protection against corrosion.

(a) BLISTERS AND PEELING

Two distinct types of blisters were observed: (a) Small blisters from which products of corrosion exuded, and (b) large blisters from which there was no exudation. As these occurred under entirely different conditions, they will be considered separately.

Blisters of the first type (fig. 5) appeared chiefly on the chromium-plated specimens, and were most common in marine locations, especially Sandy Hook. Initially, they were very fine and barely discernible to the naked eye. In time, they increased in size, and rust appeared at the apex of each. Microscopical examination showed that rust was always present. When some of these blisters were dissected under the microscope, rust was plainly evident on the underlying steel.

These facts indicate that these blisters were the result and not the cause of rusting. Apparently a fine pore in the coating permitted the exposed steel to corrode. If the pore were sufficiently fine, the initial products of corrosion might seal the opening. Any corrosion that followed would then develop pressure and tend to lift the coating to form a small blister. Continued corrosion would subsequently cause the products of corrosion to exude from the pore.

This explanation of the formation of these blisters raises several questions, namely, (a) the conditions that cause pores in a plated coating, (b) the effect of adherence of the coatings on their tendency to blister, and (c) the climatic factors that may foster blistering. It is well known that pores in the coating may be caused by defects in the base metal, by the methods of cleaning, by suspended particles in the plating bath, or by the liberation of gas on the cathode, in the latter case with the formation of visible pits. There is good reason to believe that these deposits were less porous than average commercial deposits of the same thickness. The steel was of high quality, with a good finish. It required very little cleaning or pickling to remove scale, but it was pickled to etch the surface. The solutions were made from relatively pure chemicals and were filtered. Hydrogen peroxide was added to the nickel baths so as to practically eliminate visible pits. There is no known way of completely preventing porosity, which is apparently characteristic of all plated coatings of the usual thickness.

The conditions of preparation and plating were adjusted so as to produce "perfect" adherence, that is, it was impossible to detach the coatings by any mechanical test. It is recognized that these tests

FIGURE 5.—*Small blisters observed after long exposure of many chromium-plated specimens, especially in marine locations.* ×5.

The bright spots are blisters, while the dark spots are rust that usually followed the blistering.

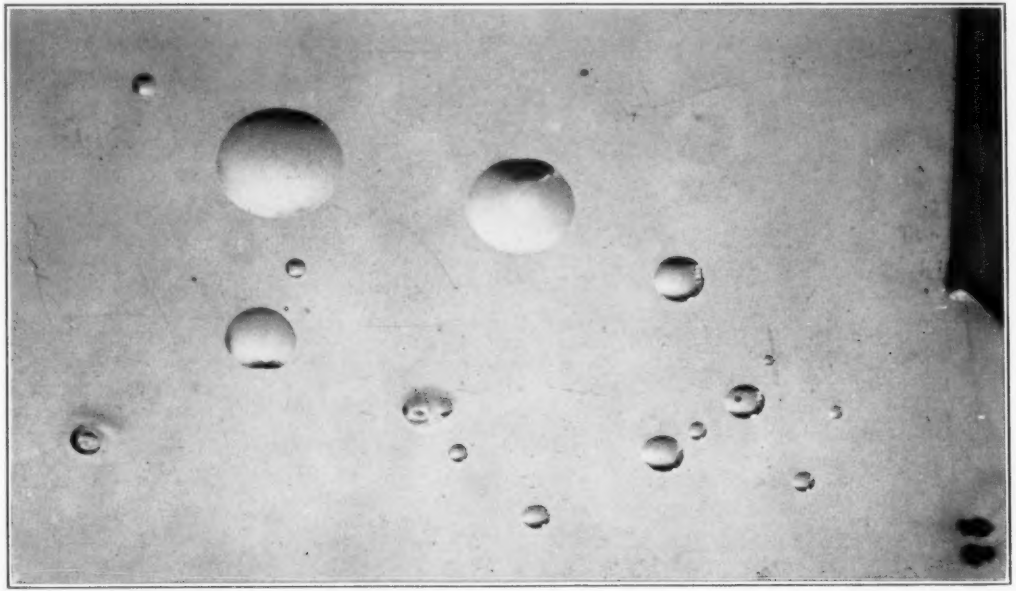

FIGURE 6.—*Large blisters that formed on storage of many of the specimens with a zinc or cadmium layer under the nickel.* Natural size.

are of limited value, and that there may have been undetectable differences in the degree of adhesion of the coatings.

The fact that these blisters occurred most frequently in marine locations indicates that they are characteristic of very rapid corrosion of the steel, which is more likely to fill up minute pores than is slower corrosion. Their more common occurrence at Sandy Hook suggests that they form most readily in a combined marine and industrial atmosphere. Their more frequent occurrence on chromium-plated specimens suggests that the adherence of the nickel coatings may have been decreased by the process of applying the chromium. The fact that they were more pronounced on specimens "102" that had been cathodically pickled (which was the only set that blistered badly in New York and Pittsburgh) suggests that their formation was fostered by hydrogen absorbed in the steel.

Another evidence that these blisters were the result of rust, is that in severe locations they finally merged to form large areas. When the coating was peeled from these a mass of rust was exposed.

Consideration has been given to these small blisters, because they were more pronounced than on most commercial plating that has rusted in service, though they have since been observed on several automobile radiators and bumpers. It is probable that their marked occurrence on these test specimens was caused by the more severe conditions of continuous exposure.

Blisters of the second type (fig. 6) appeared only on specimens that had zinc or cadmium under the nickel, and especially if copper was also present. These large blisters sometimes formed in storage before exposure, and showed no enlargement or corrosion on subsequent long exposure. When these were opened, it was found that part of the zinc or cadmium adhered to both the steel and the nickel, and there was no evidence of corrosion within the blister. It appears probable that these blisters were formed by the escape from the steel of hydrogen that was absorbed during the pickling or plating operations. While no exact data are available, it is probable that hydrogen penetrates less readily through zinc or cadmium than through steel, nickel, or chromium. The pressure developed by the hydrogen trying to escape through the zinc or cadmium was apparently sufficient actually to split the coating of soft metal. (This is an illustration of "perfect" adherence, that is, adherence equal to the strength of the weakest member of the combination.) This type of blistering was neither a cause nor effect of corrosion, though it is of course objectionable. It is a least possible that it might be eliminated by changes in the procedure that would reduce the hydrogen content of the steel.

(b) STAINS

As previously noted, black films were observed in New York and Pittsburgh. Apparently these were simply the result of rust which took the form of black magnetic oxide of iron.

White stains were observed to some extent on all the coatings that contained a layer of either zinc or cadmium. They were probably carbonates or basic sulphates of these metals, produced by their corrosion through pores in the outer layers. In general, more white stains were produced with zinc than with cadmium.

(c) CRACKS

The presence of very fine cracks in chromium deposits has been frequently reported. On exposure, these cracks sometimes became distinctly visible, but only occasionally and after long exposure did rust appear in the cracks. There was no evident relation between the development of these cracks and the conditions of chromium deposition or the protective value of the coatings.

V. SUMMARY OF EXPOSURE TESTS

1. CONCLUSIONS

(1) The protective value of nickel coatings depends almost entirely on their thickness. At least 0.0005 in. (0.013 mm) is required for good protection under mild conditions, and at least 0.001 in. (0.025 mm) for severe conditions.

(2) The conditions of nickel deposition and of the cleaning and pickling have no marked effects on the protective value.

(3) The presence of a layer of copper reduces the protective value of thin nickel deposits under all conditions, and of thick deposits under severe conditions. If chromium is also present, the copper has very little harmful effect in thick deposits. If the copper layer is buffed, the protective value of the composite coating is increased.

(4) A very thin deposit of chromium, such as 0.00001 in. (0.00025 mm), sometimes reduces the protective value, especially of pure nickel deposits. Chromium coatings about 0.00002 to 0.00003 in. (0.0005 to 0.0008 mm) add very little to the protective value, but maintain their bright appearance owing to their resistance to tarnish. Relatively thick chromium coatings, from 0.00005 to 0.0001 in. (0.0013 to 0.0025 mm), improve the protection against corrosion, especially in an industrial atmosphere.

(5) The protective value of chromium over nickel or composite coatings is somewhat improved by using a bath with a high ratio, $\frac{\text{g/l } CrO_3}{\text{g/l } SO_4}$, such as 200. Deposits produced at 35 C (95 F) are slightly superior to those made at somewhat higher temperatures.

(6) The use of zinc under nickel makes the protective value less than that of either metal alone. Cadmium has very little effect under nickel.

(7) The use of zinc or cadmium under nickel tends to produce white stains and blisters.

2. RELATION TO OTHER INVESTIGATIONS

There have been very few comparable exposure tests of metals plated with known thicknesses of copper, nickel, or chromium. The conclusions of E. M. Baker [13] regarding effects of thickness and of multiple coatings were based largely on accelerated tests such as the salt spray. The reported [14] superiority of nickel deposits produced at a low pH was based on specimens that were all plated with chromium and exposed at one location (inland near Miami, Fla.). The results of the present study also show a slight superiority of the plates

[13] J. Soc. Automotive Eng. 15,127(1924).
[14] W. M. Phillips, Trans. Am. Electrochem. Soc. 59,393(1931).

with nickel deposited at a low pH when coated with chromium, but not without the chromium.

Pierre Jacquet [15] made exposure tests of numerous plated steel specimens on the roof of a building in Paris. In general his conclusions are consistent with those of this study. He found that no appreciable protection was furnished by nickel deposits less than 0.008 mm (0.0003 in.), and that the conditions of nickel deposition had little effect. He reported that very thin chromium deposits decreased the protective value and he advised the use of not less than 0.00067 mm (0.000027 in.) of chromium. He found that the presence of cadmium as an intermediate layer led to peeling of the final layers. He advised the use of coatings consisting of Ni, Cu, Ni, Cr, though he did not include any in his tests.

Assistance has been received from too many persons to permit individual acknowledgments. The authors are especially indebted to their associates at the National Bureau of Standards for their advice and assistance; to the members of the joint inspection committee and other interested persons for cooperation in the inspections and the interpretation of the results; and to numerous firms that supplied the anodes and chemicals used in plating and the steel for the specimens and exposure racks.

Washington, July 20, 1934.

[15] Bul. Soc. Française Electriciens [5]2,631(1932).

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HEATS OF COMBUSTION OF RUBBER AND OF RUBBER-SULPHUR COMPOUNDS

By R. S. Jessup and A. D. Cummings

ABSTRACT

Measurements with a bomb calorimeter have been made of the heats of combustion of samples of rubber purified by various methods, and of compounds of rubber and sulphur containing up to 32 percent sulphur. In the calorimetric combustion experiments on rubber-sulphur compounds, an amount of aqueous Na_2CO_3 or NaOH more than sufficient to react with the products of combustion containing sulphur was placed in the bomb before each experiment in order to obtain a definite final state for the system.

The average value obtained for the heat of combustion of ether-soluble rubber in gaseous oxygen to form gaseous carbon dioxide and liquid water at a temperature of 30° C and a constant pressure of one atmosphere is 45,207 international joules per gram (weight in vacuo). The estimated uncertainty of this value is 0.2 percent. The average values obtained for ether-insoluble and total rubber are lower by 0.9 and 0.4 percent, respectively, than the value for ether-soluble rubber. The samples of ether-insoluble and total rubber contained considerably more ash than those of ether-soluble rubber, and there is some evidence which indicates that the ash does not represent the total inert impurity in the samples. It is possible that if the inert impurity could be determined with greater accuracy the values for the heats of combustion of the different kinds of rubber would be very nearly the same.

The values obtained for the heats of combustion of compounds of rubber and sulphur in gaseous oxygen to form gaseous carbon dioxide, gaseous sulphur dioxide, and liquid water at a temperature of 30° C and a constant pressure of one atmosphere may be represented by the empirical equation:

$$Q_c = 45{,}200 - 37{,}823\ m$$

where Q_c is the heat of combustion in international joules per gram (weight in vacuo) of compound and m is the mass of sulphur per gram of compound. The average difference between observed values of heat of combustion and values calculated from this equation is 0.1 percent, and the maximum difference is 0.4 percent.

From these data on the heats of combustion of rubber and of rubber-sulphur compounds, and the data of Eckman and Rossini on the heat of combustion of sulphur, the heat of combination of rubber with rhombic sulphur at a temperature of 30° C and a constant pressure of one atmosphere, has been calculated to be 1,881 international joules per gram of sulphur, or 60.3 international kilojoules per mole of sulphur, independent of the percentage of sulphur in the compound. The estimated uncertainty of these values is 15 percent.

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I. INTRODUCTION

The work described in this paper is part of a series of investigations at the National Bureau of Standards to determine the properties of purified rubber and of compounds of purified rubber and sulphur.

Values of the heat of combustion of rubber have been reported by a number of observers, and values of the heat of combination of rubber and sulphur, determined as the difference in the heats of combustion of vulcanized and unvulcanized rubber-sulphur mixtures, have been reported by several observers. The results obtained by the various investigators are not in satisfactory agreement. The values reported in the literature for the heat of combustion of rubber vary over a range of about 4.5 percent, and the two recent sets of data on the heat of combination of rubber and sulphur differ radically, as may be seen from figure 2.

It was thought that these differences might be due, in part at least, to differences in the composition of the rubber, and that more consistent results might be obtained by using purified rubber. The data presented in this paper were obtained on samples of purified rubber and on compounds of purified rubber and sulphur prepared in connection with an investigation of the electrical properties of rubber and rubber-sulphur compounds by Scott, McPherson, and Curtis.[1]

II. PREPARATION OF SAMPLES

Two of the samples of purified rubber, designated as samples E_{39} and E_{40}, were prepared by the method described by McPherson.[2] Briefly, this consists in digestion of latex with water at a temperature of 190° C, and extraction with water and ethyl alcohol. This process gives a material which is completely and readily soluble in ether. This method of preparation of rubber is designated as "steam purification" in this paper.

The remaining samples of purified rubber were prepared by the method described by Smith, Saylor, and Wing.[3] This method involves the use of trypsin for the removal of protein, and is designated as "trypsin purification." It was developed with the aim of preserving the structure of the rubber hydrocarbon as it exists in the latex. Rubber prepared by this method consists of about 75 percent ether-soluble and 25 percent ether-insoluble rubber, and is designated in this paper as "total" rubber. Samples of ether-soluble and ether-insoluble rubber were obtained from trypsin purified rubber by ether extraction. When the two fractions are separated by this method, the insoluble impurities are concentrated in the ether-insoluble fraction.

All of the rubber-sulphur compounds were prepared from steam purified rubber. The specimens used in heat of combustion measurements were vulcanized between aluminum plates for 40 hours at a temperature of 141° C in an autoclave containing carbon dioxide under a pressure of about 3 atmospheres. Details of compounding the rubber and sulphur have been reported by Scott, McPherson,

[1] BS J. Research 11, 173(1933); RP585.
[2] BS J. Research 8, 751(1932); RP449.
[3] BS J. Research 10, 479(1933); RP544.

and Curtis.[4] The residual uncombined sulphur was less than 0.1 percent of the total compound, except when the total sulphur amounted to 32 percent. In this case uncombined sulphur was present in varying amounts up to 0.8 percent. The effect on the measured heat of combustion of 0.8 percent uncombined sulphur is about 0.05 percent.

III. HEATS OF COMBUSTION

1. APPARATUS AND METHODS

The calorimetric apparatus and methods employed in this work were essentially the same as those used by Jessup and Green,[5] and are described in the reference cited. The "Illium" bomb used is of the type devised by Parr, and has a capacity of 377 cm^3.

Temperatures were measured by means of a platinum resistance thermometer of the calorimetric type described by Sligh,[6] used in conjunction with the Wheatstone bridge described by Waidner, Dickinson, Mueller, and Harper.[7]

The heat capacity of the calorimeter was determined by several combustions of benzoic acid (National Bureau of Standards Standard Sample No. 39e). The value used for the heat of combustion of the benzoic acid is that recently determined in this laboratory,[5] namely, 26,419 international joules per gram (weight in vacuo), when the reaction is referred to 25° C, the initial oxygen pressure is 30 atmospheres absolute, and the masses of benzoic acid and water placed in the bomb are each 3 grams per liter of bomb volume. The precision of the heat capacity determinations was about 0.03 percent. Details of the procedure followed in heat of combustion measurements are given in the reference cited.

2. PURIFIED RUBBER

The samples of rubber were contained in a platinum crucible, and burned at constant volume in oxygen under an initial pressure of 30 atmospheres. One cm^3 of water was placed in the bomb before each experiment. The oxygen, before being admitted to the bomb, was passed through a tube containing copper oxide heated to about 750° C in order to remove combustible impurities.

The results obtained on samples of purified rubber are summarized in table 1. The value given for each sample is the mean of at least two determinations. The average deviation of the results of individual experiments on any one sample from the mean for that sample is 0.04 percent, and the maximum deviation is 0.14 percent.

[4] BS J. Research **11**, 173(1933); RP585.
[5] Heat of combustion of benzoic acid, J. Research NBS **13** (October 1934).
[6] BS Sci. Pap. **17**, 49(1921); S407.
[7] Bul. BS **11**, 571(1914); S241.

TABLE 1.—*Summary of results on purified rubber*

A. STEAM PURIFIED RUBBER

Sample	Heat of combustion at 30° C and a constant pressure of 1 atmosphere	Deviation from mean	Ash	Remarks
	Int. j/g	*Int. j/g*	*Percent*	
E_{40}	45, 255	+16	0. 02	Ether-soluble.
E_{39}	45, 223	−16	. 03	Do.
Mean	45, 239			

B. TRYPSIN PURIFIED RUBBER

1. Ether-soluble

E_{34B}	45, 225	+39	0. 01	Benzol-soluble.
S_3	45, 239	+53	. 14	
E_{41}(sol.)	45, 095	−91	. 11	
Mean	45, 186			

2. Ether-insoluble

S_2	44, 942	+154	0. 73	
E_{34D}	44, 457	−331	1. 85	Benzol-insoluble.
E_{41}(insol.)	44, 965	+177	. 64	
Mean	44, 788			

3. Total

E_{34}	45, 039	+4	0. 42	
E_{34A}	45, 019	−16	. 42	E_{34} exhausted at 100° C with mercury pump to constant weight. Loss 0.25 percent.
S_1	44, 890	−145	. 50	
E_{33}	45, 030	−5	. 16	9 months after preparation, acetone extracted, kept between aluminum plates.
E_{41}	45, 197	+162	. 17	
Mean	45, 035			

NOTE.—E_{34B} and E_{34D} were prepared from trypsin-purified latex-rubber which had soaked for about 3 months in C_6H_6 in the dark at room temperature.

E_{41}(sol.) and E_{41}(insol.) were prepared directly from E_{40} by ether extraction without any other solvent treatment.

All trypsin-purified samples were acetone extracted (acetone removed several days in vacuum dessicator) just before final drying previous to making combustion experiments.

Samples S_1, S_2, and S_3 were prepared by W. H. Smith.

The method of calculating the results is illustrated in table 2. The observed heat of combustion at 30° C ($-\Delta U_B$) was reduced by the method described by Washburn [8] to the difference ($-\Delta U_R$) in the internal energies of the initial and final systems when the rubber and pure gaseous oxygen of the initial system, and the pure gaseous carbon dioxide and pure liquid water of the final system are each under a pressure of 1 atmosphere at 30° C. The heat of combustion at a constant pressure of 1 atmosphere was then calculated by adding to the value of $-\Delta U_R$ the value of $-\Delta(pv)$ for the reaction at a pressure of 1 atmosphere (75 joules per gram of rubber).

[8] BS J. Research **10**, 525(1933); RP546.

TABLE 2.—*Calculation of heat of combustion of purified rubber from observed data*

Experiment 8

Sample	E_{40}
Method of purification	Steam
Initial oxygen pressure	30.0 atm
Mass of sample (wt in vacuo)	1.0072 g
Mass of ash	.0002 g
Mass of rubber	1.0070 g
Heat evolved	45,604. int. joules
Correction for:	
Firing energy	−23. int. joules
Formation of HNO_3	−77. int. joules
Unburned carbon	0. int. joules
Heat produced by combustion of rubber	45,504. int. joules
Observed heat of combustion ($-\Delta U_B$)	45,187. int. joules/g
Reduction to $p=1$ atm	−15. int. joules/g
Energy change for reaction at 1 atmosphere ($-\Delta U_R$)	45,172. int. joules/g
Heat of combustion of ash-free rubber at const. $p=1$ atm	45,247. int. joules/g

After some of the experiments, there remained in the crucible a small quantity (as much as 0.3 mg in some cases) of unburned carbon, the amount of which was determined by weighing. Correction for this unburned carbon was made, using the approximate value 33,000 joules per gram for the heat of combustion of carbon.

The gaseous products of combustion of several samples were examined for carbon monoxide using the method described by Eiseman, Weaver, and Smith.[9] No carbon monoxide was found even when unburned carbon was left in the crucible.[10]

The thermal effect of solution of oxygen in the rubber samples prior to ignition in the combustion experiments was determined as follows: The empty bomb was placed in the calorimeter, the temperature of which was very nearly the same as that of the jacket. Oxygen was then slowly admitted to the bomb through a coil of tubing immersed in the jacket water, and the temperature rise of the calorimeter was measured. The experiment was then repeated with seven 1-gram samples of steam-purified rubber in the bomb. The final oxygen pressure in the bomb was 30 atmospheres in each experiment. The valve which controlled the flow of oxygen was located between the oxygen supply tank and the coil of tubing which was immersed in the jacket water, so that practically all of the throttling of the oxygen took place before it entered this coil. Corrections were applied for heat interchange between calorimeter and jacket and for heat of stirring of the water in the calorimeter. The results obtained with rubber in the bomb were corrected to take account of the smaller volume available for the oxygen, and for the increased heat capacity of the system due to the presence of the rubber. The finally corrected temperature rise of the calorimeter in the experiments with the empty bomb was the same, within the limits of the precision of the measurements, as the corrected temperature rise in the experiments in which rubber was placed in the bomb. This indicates that there is no appreciable thermal effect arising from solution of oxygen in the rubber. The precision of the measurements, as indicated by the reproducibility of the results, was sufficiently high to detect an effect which would have caused an error of 0.01 percent in the measured heat of combustion of the rubber.

[9] B8 J. Research 8,669(1932); RP446.
[10] The tests for carbon monoxide were made by C. Creitz.

Table 1 shows that the data on ether-soluble rubber are fairly concordant, although the result for sample E_{41}(sol.), is about 0.3 percent lower than the average for the other four samples. For the total and the ether-insoluble rubbers the agreement is not so good, the spread of the results being 0.7 percent and 1.1 percent, respectively.

Although the data given in table 1 are corrected for the observed ash contents of the various samples, there is some indication that the ash does not represent the total inert impurity in the rubber, and that the differences in the observed heats of combustion of the different samples of rubber are due to this fact. If the observed heats of combustion of the various samples are plotted against the observed ash contents, the points lie approximately on a straight line as shown in figure 1. The curve indicates that the heat of combustion of a

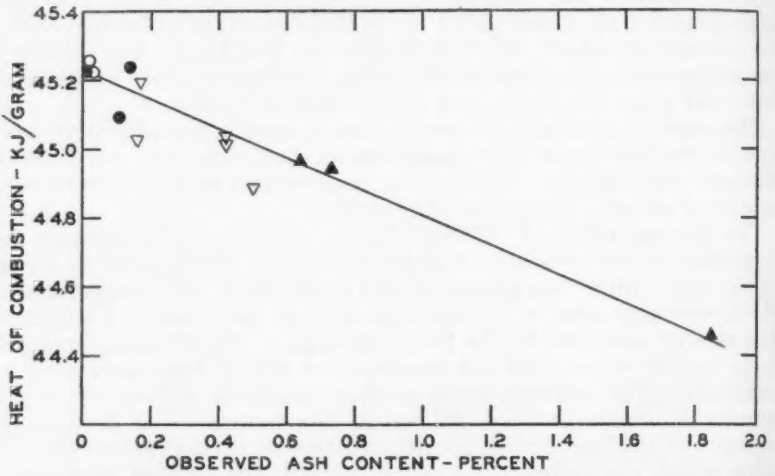

FIGURE 1.—*Observed heat of combustion of purified rubber plotted against observed ash content.*

○ Steam-purified, ether-soluble.
● Trypsin-purified, ether-soluble.
▽ Trypsin-purified, total.
▲ Trypsin-purified, ether-insoluble.

sample containing p percent ash is lower by about p percent than that of a sample containing no ash. This might be explained by assuming that the inert impurity consists of approximately equal parts by weight of volatile and nonvolatile materials. The observed ash content would then be only half of the total inert impurity in the sample of rubber.

Two or three determinations of benzol-insoluble matter in several samples of rubber were in satisfactory agreement with the ash determinations. This fact does not necessarily prove that the above assumption in regard to volatile inert impurity is incorrect, since such impurity might be both volatile and soluble in benzol. It is possible that if the inert impurity could be determined with greater accuracy, the values obtained for the heats of combustion of the different kinds of rubber would be very nearly the same.

The differences between the results for the various samples may also be partly due to chemical combination of ash or of oxygen with

the rubber. It would be very desirable to investigate these various possibilities further, but it has not yet been possible to carry out this work.

The consistency of the results for samples of ether-soluble rubber prepared in different ways indicates that the average value for the heat of combustion of this material, 45,207 international joules per gram (weight in vacuo) at a temperature of 30° C and a constant pressure of 1 atmosphere, is not in error by more than 0.2 percent.

If the atomic weights of carbon and hydrogen are taken as 12.00 and 1.0078, and if it is assumed that rubber is the compound $(C_5H_8)_x$, the value obtained for the heat of combustion of ether-soluble rubber at a temperature of 30° C and a constant pressure of 1 atmosphere is $(3{,}077 \pm 6)x$ international kilojoules per mole.[11] The temperature coefficient of the heat of combustion is so small that this figure is practically unchanged by reduction to 25° C.

Using this value for the heat of combustion of rubber, and the values given in table 4 for the heats of formation of CO_2 and water, the heat of formation of ether-soluble rubber, at a temperature of 25° C and a constant pressure of 1 atmosphere, from gaseous hydrogen and carbon in the form of diamond is found to be $(42 \pm 6)x$ international kilojoules per mole of $(C_5H_8)_x$.

3. RUBBER-SULPHUR COMPOUNDS

The first two experiments on rubber-sulphur compounds were performed in the same way as the experiments on purified rubber, except that 10 cm^3 of water were placed in the bomb to absorb the products of combustion containing sulphur. Examination of the products of combustion showed that part of the sulphur had been oxidized to SO_2 and part to SO_3, and that about half of the SO_3 was in the liquid and half in the gas phase. As it was not known how much water was associated with the SO_3 in the gas phase, it was not possible to calculate from the observed results, the heat of combustion of the sample corresponding to any definite final state.

In each of the next three experiments, slightly more than enough normal solution of NaOH was placed in the bomb to combine with the products of combustion containing sulphur. In the remaining experiments, pure sodium carbonate was placed in the bomb, the amount being 5 to 10 percent in excess of that required to combine with the products of combustion containing sulphur. The sodium carbonate was dissolved in distilled water, the amount of water varying from 2 to 20 cm^3 in the various experiments. The combustion was carried out in the same manner as for purified rubber. The time required to reach a steady state after the combustion was from 40 to 60 minutes in the experiments on rubber-sulphur compounds, as compared with 4 or 5 minutes when purified rubber was burned.

Tests showed that when a solution of NaOH or Na_2CO_3 was placed in the bomb before an experiment, the washings from the bomb after combustion contained only Na_2SO_4, $NaNO_3$, and a little $NaHCO_3$ formed by reaction of CO_2 and water with the excess NaOH or Na_2CO_3. No Na_2SO_3 was found in the bomb washings, although when no NaOH or Na_2CO_3 was placed in the bomb, some SO_2 was

[11] Values given for the uncertainty of data obtained in this investigation are based partly on the consistency of the data and partly on estimates of the probable effect of systematic errors.

found. A possible explanation of this is that minute traces of copper may have acted as a catalyst in increasing the velocity of oxidation of Na_2SO_3 to Na_2SO_4. It has been shown by Titoff [12] and by Mack, Osterhof, and Kramer [13] that the velocity of this reaction is greatly increased by very small amounts of copper.

The amounts of Na_2SO_4, $NaNO_3$, and $NaHCO_3$ in the bomb washings were determined for each experiment as follows: The washings were filtered, evaporated to dryness on the steam bath, dried 2 hours at 150° C, and the residue weighed. The residue was then dissolved in distilled water to make 100 ml of solution. Ten ml of this solution were evaporated to dryness and used to determine the nitrate by the phenoldisulphonic acid method used in water analysis. The remaining solution, containing in addition to the substances mentioned above a little Na_2CO_3 formed by decomposition of the $NaHCO_3$ in drying, was titrated with $N/100$ acid and the phenolphthalein and methyl orange end-points recorded. From the data obtained, the amounts of Na_2CO_3, $NaHCO_3$, and $NaNO_3$ were calculated, and the amount of Na_2SO_4 found by difference. The amount of $NaHCO_3$ reported was the amount found plus the $NaHCO_3$ equivalent of the Na_2CO_3 found.

TABLE 3.—*Calculation of the heat of combustion of a rubber sulphur compound*

Experiment 10

Sample	$E_{28}-26$
Initial oxygen pressure	30.1 atm
Mass of water in bomb	20.0 g
Mass of Na_2CO_3	1.066 g
Mass of Na_2SO_4	1.1514 g
Mass of $NaHCO_3$	0.3116 g
Mass of $NaNO_3$	0.0023 g
Mass of sample	1.0020 g
Mass of ash	.0005 g
Mass of compound, m	1.0015 g
Mass of sulphur	.2599 g
Mass of C_5H_8	.7416 g
Percent sulphur	25.95
$-m\,\Delta U_B$	38, 140. int. joules
q_i	23. int. joules
$-\Delta U_D$	38. int. joules
$-\Delta U_{Gas}$	7. int. joules
$-\Delta U_{Na_2SO_4}$	2, 689. int. joules
$-\Delta U_{NaHCO_3}$	57. int. joules
$-\Delta U_{NaNO_3}$	2. int. joules
$-m\,\Delta U_B$	35, 324. int. joules
$-\Delta U_B$	35, 271. int. joules/g
$-\Delta(pv)$	57. int. joules/g
Q_c	35, 328. int. joules/g

Table 3 illustrates the method used in calculating the heats of combustion of the rubber-sulphur compounds when Na_2CO_3 was used to react with the products of combustion of the sulphur. The item, $-m\Delta U_B$, in this table is the heat evolved in the actual bomb process when m grams of rubber-sulphur compound are burned, the initial system consisting of the solid compound, gaseous oxygen containing a small amount of nitrogen, and a liquid aqueous solution of Na_2CO_3 and oxygen, all at 30° C and under a pressure of 30 atmospheres; and the final system consisting of a gaseous mixture of oxygen and carbon dioxide, and a liquid solution of O_2, CO_2, Na_2SO_4, $NaHCO_3$, and $NaNO_3$, all at 30° C and under the pressure existing in the bomb

[12] Z. Physik. Chem. **45**, 641 (1903).
[13] J. Am. Chem. Soc. **45**, 617 (1923).

at the end of the experiment. The quantity, $-m\Delta U_R$, is the internal energy of the initial system minus that of the final system when the initial system consists of the solid rubber-sulphur compound and gaseous oxygen, both at 30° C and under a pressure of one atmosphere; and the final system consists of liquid water, gaseous CO_2, and gaseous SO_2, each at 30° C and under a pressure of 1 atmosphere. The heat of combustion of the compound at constant pressure of 1 atmosphere (Q_C) is obtained by adding to $-\Delta U_R$ the value of $-\Delta(pv)$, the difference in the product of pressure and volume of the initial and final systems at 30° C and a pressure of 1 atmosphere.

The value of $m\Delta U_R$ is obtained from that of $m\Delta U_B$ by means of the relation

$$m\Delta U_R = m\Delta U_B - (-q_1 + \Delta U_D + \Delta U_{Gas} + \Delta U_{Na_2SO_4} + \Delta U_{NaHCO_3} + \Delta U_{NaNO_3}) \quad (1)$$

where the first 3 terms in parentheses are defined as follows:

q_1 = the energy used in firing the charge.

ΔU_D = the increase in internal energy of the system due to solution of CO_2 in the aqueous solution in the bomb at the end of the experiment.

ΔU_{Gas} = the increase in internal energy for the reaction which takes place in the bomb minus the increase in internal energy for a reaction identical with that which takes place in the bomb except that the gaseous oxygen of the initial system and the gaseous oxygen and carbon dioxide of the final system are each at 30° C and under a pressure of 1 atmosphere.

The values of ΔU_D and ΔU_{Gas} were calculated by the methods given by Washburn,[14] with such modifications as were necessary on account of the fact that the material burned contained sulphur in addition to carbon and hydrogen.

The items $\Delta U_{Na_2SO_4}$, ΔU_{NaHCO_3}, and ΔU_{NaNO_3} are defined differently depending on whether Na_2CO_3 or NaOH was placed in the bomb to react with the products of combustion of the sulphur. If Na_2CO_3 was placed in the bomb, these items are the internal energies of the final systems minus those of the initial systems in the following reactions, respectively:

$$Na_2CO_3(XH_2O) + SO_2(gas) + 1/2\ O_2(gas) = Na_2SO_4(YH_2O) + CO_2(gas) \quad (2)$$

$$Na_2CO_3(XH_2O) + H_2O(liq.) + CO_2(gas) = 2NaHCO_3(YH_2O) \quad (3)$$

$$Na_2CO_3(XH_2O) + N_2(gas) + 5/2\ O_2(gas) = 2\ NaNO_3(YH_2O) + CO_2(gas) \quad (4)$$

If NaOH was placed in the bomb, the items $\Delta U_{Na_2SO_4}$, ΔU_{NaHCO_3}, and ΔU_{NaNO_3} are respectively, the internal energies of the final systems minus those of the initial systems in the following reactions:

$$2\ NaOH(XH_2O) + SO_2(gas) + 1/2\ O_2(gas) = Na_2SO_4(YH_2O) + H_2O(liq.) \quad (5)$$

$$NaOH(XH_2O) + CO_2(gas) = NaHCO_3(YH_2O) \quad (6)$$

[14] BS J. Research **10**, 525(1933); RP546.

$$2\,NaOH(XH_2O) + N_2(gas) + 5/2\,O_2(gas) = 2\,NaNO_3(YH_2O) + H_2O(liq.) \quad (7)$$

In all the reactions 2 to 7 inclusive, each of the reactants and products is under a pressure of 1 atmosphere at 30° C, and the masses are those actually involved in the reactions which took place in the bomb.

The difference in the energies of the initial and final systems at 30° C in the reactions represented by equations 2 to 7 were calculated from the heats of formation at 18° C of each of the compounds involved, data on the specific heats of all of the substances involved, and data on the densities of the gases at 30° C and atmospheric pressure. The values used for the heats of formation of the compounds are given in table 4.

TABLE 4.—*Values used for the heats of formation of various compounds at 18° C*

Compound	Heat of formation [1]	Compound	Heat of formation [1]
	Int. kilojoules/mole		*Int. kilojoules/mole*
CO_2 (gas)	[2] 395.12	NaOH (100 H_2O)	468.95
SO_2 (gas)	296.71	NaOH (50 H_2O)	469.30
H_2O (liq.)	286.01	Na_2SO_4 (400 H_2O)	1,383.57
Na_2CO_3 (400 H_2O)	[2] 1,152.59	Na_2SO_4 (200 H_2O)	1,384.62
Na_2CO_3 (200 H_2O)	[2] 1,153.64	Na_2SO_4 (100 H_2O)	1,386.56
Na_2CO_3 (100 H_2O)	[2] 1,155.39	Na_2SO_4 (50 H_2O)	1,389.35
Na_2CO_3 (50 H_2O)	[2] 1,158.07	$NaNO_3$ (400 H_2O)	449.22
Na_2CO_3 (25 H_2O)	[2] 1,161.25	$NaHCO_3$ (200 H_2O)	[2] 930.0

The data in this table were supplied by F. D. Rossini, who has been critically reviewing the literature on thermochemistry.

[1] Heat of formation from diamond, gaseous oxygen, etc.

The heats of combustion of the purified ether-soluble rubber and of the rubber-sulphur compounds in gaseous oxygen to form gaseous CO_2, gaseous SO_2, and liquid water, at a temperature of 30° C and a constant pressure of 1 atmosphere can be represented within the limits of experimental error by the empirical equation:

$$Q_c = 45{,}200 - 37{,}823m \quad (8)$$

where Q_c is the heat of combustion in international joules per gram mass (weight in vacuo) of compound, and m is mass of sulphur per gram of compound. The average difference between observed values of the heats of combustion of rubber-sulphur compounds, and values calculated from this equation is 0.1 percent, and the maximum difference is 0.4 percent.

IV. HEAT OF COMBINATION OF RUBBER WITH SULPHUR

The heat of combination of rubber with sulphur at 30° C and atmospheric pressure can be calculated from the heats of combustion of the rubber-sulphur compounds and of unvulcanized rubber-sulphur mixtures. The heats of combustion of unvulcanized mixtures can

be calculated from the heats of combustion of rubber and rhombic sulphur by means of the relation:

$$Q_M = mQ_s + (1-m)\ Q_R \tag{9}$$

where Q_R, Q_s, and Q_M are respectively, the heats of combustion per gram of rubber, sulphur, and the unvulcanized mixture of rubber and sulphur, and m is the mass of sulphur in a one-gram sample of the mixture.

The heat of combustion of sulphur has been determined by Eckman and Rossini,[15] who give for the heat of the reaction:

$$S(\text{rhombic}) + O_2(\text{gas}) = SO_2(\text{gas})\ (25°C) \tag{10}$$

the value 296.79 ± 0.20 international kilojoules per mole (32.065g) of sulphur, and for the temperature coefficient of the heat of reaction the value 12 joules per degree per mole. These data yield the value 9258 ± 6 international joules per gram of sulphur for the heat of combination of rhombic sulphur and gaseous oxygen to form gaseous SO_2 at 30° C.

Using this value for Q_s and 45,200 international joules per gram for Q_R, equation (9) becomes

$$Q_M = 45{,}200 - 35{,}942m \text{ int. joules per gram} \tag{11}$$

The calculated heat of combination of rubber and sulphur at 30° C is then given by the difference between equations 8 and 11, or

$$Q_V = Q_M - Q_C = (1881 \pm 300)m \text{ int. joules} \tag{12}$$

where Q_V is the heat evolved when m gram of rhombic sulphur and $(1-m)$ gram of rubber combine at 30° C and under a constant pressure of 1 atmosphere, to form 1 gram of vulcanized rubber.

According to equation 12 the heat of combination of sulphur with rubber is independent of the amount of rubber (provided the sulphur does not exceed 32 percent of the total) and is equal to 1881 ± 300 international joules per gram of sulphur, or 60.3 ± 9.6 international kilojoules per mole of sulphur.

In table 5 are given the observed heats of combustion of rubber and of the rubber-sulphur compounds, together with values calculated from equation 8; and derived values of the heat of combination of rubber and sulphur, together with values calculated from equation 12. The derived values of heat of combination of rubber and sulphur are obtained from the relation:

$$Q_V(\text{der}) = Q_M(\text{calc}) - Q_C(\text{obs}) \tag{13}$$

[15] BS J. Research **3**,597(1929);RP111.

TABLE 5.—*Observed and calculated values of heats of combustion of purified sol rubber and rubber-sulphur compounds, and heats of vulcanization of the compounds, at a constant pressure of one atmosphere at 30° C.*

Sample	Ash	Sulphur in ash-free material	Q_c				Q_v			
			Observed	Calculated (equation 8)	Obs-calc	$100\frac{\text{Obs-calc}}{\text{calc}}$	Derived (equations 11, 13)	Calculated (equation 12)	Der-calc	$100\frac{\text{Der-calc}}{\text{calc}}$
	Percent	*Percent*	*Int.j/g*	*Int.j/g*	*Int.j/g*	*Percent*	*Int.j/g*	*Int.j/g*	*Int.j/g*	*Percent*
E_{40}	0.02	0.00	45255	45200	+55	+0.12				
E_{39}	.03	.00	45223	45200	+23	+.05				
E_{34B}	.01	.00	45225	45200	+25	+.06				
S_3	.14	.00	45239	45200	+39	+.09				
E_{41} (sol.)	.11	.00	45095	45200	−105	−.23				
E_{29}–2	.15	2.06	44381	44421	−40	−.09	79	39	+40	+102
Do	.15	2.09	44412	44409	+3	+.01	37	39	−2	−5
E_{31}–6	.10	6.05	42914	42912	+2	.00	112	114	−2	−2
Do	.10	6.14	42928	42878	+50	+.12	65	116	−51	−43
E_{29}–10	.13	10.06	41318	41395	−77	−.19	266	189	+77	+41
Do	.13	10.10	41311	41380	−69	−.17	259	190	+69	+36
E_{14}–16	.08	16.03	39163	39137	+26	+.07	275	301	−26	−9
Do	.08	16.07	39148	39122	+26	+.07	276	302	−26	−9
E_{28}–20	.03	20.03	37612	37624	−12	−.03	389	377	+12	+3
Do	.03	20.20	37554	37560	−6	−.02	386	380	+6	+2
E_{28}–26	.05	25.90	35433	35405	+28	+.08	458	487	−29	−6
Do	.05	25.95	35328	35385	−57	−.16	545	488	+57	+12
E_{28}–32	.07	31.33	33262	33350	−88	−.26	677	589	+89	+15
Do	.07	31.71	33203	33206	−3	−.01	600	597	+3	+1
Do	.07	31.88	33103	33142	−39	−.12	639	600	+39	+7
Do[1]	.07	32.00	33058	33097	−39	−.12	641	602	+39	+6
Do[1]	.07	32.09	33187	33059	+128	+.39	476	604	−128	−21
Do[1]	.07	32.17	33116	33032	+84	+.25	521	605	−84	−14

[1] NaOH was placed in the bomb to react with the products of combustion containing sulphur in these experiments. Na_2CO_3 was used for this purpose in all other experiments on rubber-sulphur compounds.

V. PREVIOUS WORK

Measurements of the heat of combustion of rubber have been made by Weber,[16] Kirchoff and Matulke,[17] Blake,[18] Messenger,[19] and Hada, Fukaya, and Nakajima.[20] The results reported by these investigators are given in the second column of table 6. Conversion to joules per gram was made by means of the relation

$$1 \text{ calorie} = 4.183_3 \text{ international joules},$$

and the values of heat of combustion at constant pressure were obtained by adding 75 joules per gram to the values of heat of combustion at constant volume. The results are not reduced to standard initial and final states, as recommended by Washburn,[21] since this reduction would change the figures given by only a negligible amount.

TABLE 6.—*Values of the heat of combustion of rubber reported by various observers*

Observer	Constant volume	Constant pressure
	Cal/g	*Int. joules/g*
Weber	10,669	44,710
Kirchoff and Matulke	10,700	44,840
Blake	10,547	44,200
Messenger	10,970	45,970
Hada, Fukaya, and Nakajima	10,495	43,980
Present work (total rubber)		45,040

[16] The Chemistry of India Rubber, p. 107, J. B. Lippincott and Co., Philadelphia (1903).
[17] Ber.Deut. Chem. Ges. **57B**, 1266(1924).
[18] Ind. Eng. Chem. **22**, 737(1930).
[19] Rubber Chem. Tech. **3**, 24(1930).
[20] Rubber Chem. Tech. **4**, 507(1931).
[21] BS J. Research **10**, 525 (1933); RP546.

It will be seen from table 6 that the results obtained by the various observors are distributed over a range of about 4.5 percent. This is not surprising in view of the fact that most of the results were obtained on rubber which contained considerable amounts of impurities, and in view of the differences in the results obtained in the present work on different samples containing much smaller amounts of impurities.

Measurements of the heat of combination of rubber and sulphur have been made by Blake,[22] and by Hada Fukaya, and Nakajima.[23] The results obtained by these observers, together with the results of the present work, are shown in figure 2.

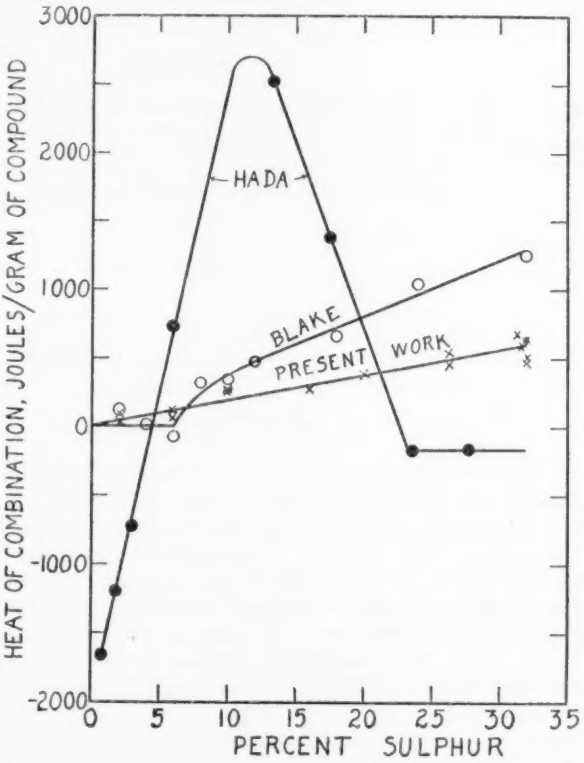

FIGURE 2.—*Heat of combination of rubber with rhombic sulphur.*

Blake determined the heat of combination as the difference in the heats of combustion of vulcanized and unvulcanized samples. No details of calorimetric measurements and no analyses of the products of combustion are given.

Hada, Fukaya, and Nakajima determined heats of combustion of vulcanized compounds and calculated the heats of combustion of unvulcanized mixtures from their own value for the heat of combustion of rubber and Thomsen's data on the heat of combustion of sulphur. Resins were removed from the rubber by acetone extraction, and corrections were applied for the heat of reaction of sulphur with protein. No details are given regarding calorimetric measurements. As may be seen from figure 2, the results obtained differ radically from those of Blake and those of the present work.

In conclusion, the authors wish to acknowledge their indebtedness to A. T. McPherson, under whose general direction this work was done.

WASHINGTON, June 25, 1934.

[22] Ind. Eng. Chem. **22**, 737 (1930).
[23] Rubber Chem. Tech. **4**, 507 (1931).

U.S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP714

Part of Journal of Research of the National Bureau of Standards, Volume 13, September 1934

DRIFT OF MAGNETIC PERMEABILITY AT LOW INDUCTIONS AFTER DEMAGNETIZATION

By Raymond L. Sanford

ABSTRACT

The magnetic permeability of ferromagnetic materials at low values of induction depends upon the time which elapses between demagnetization and testing. The change may be of the order of 10 or 12 percent. In order to obtain consistent and reproducible results in testing at low inductions, a period of from 18 to 24 hours should elapse after demagnetization before the test is made.

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I. INTRODUCTION

In the standard methods of test for the magnetic properties of iron and steel adopted in 1933 [1] by the American Society for Testing Materials, two alternative methods are given for the determination of permeability and core loss at very low values of induction. It is obvious that unnecessary disputes are likely to arise unless the two methods give substantially the same results for identical specimens. In order to determine whether or not this requirement is fulfilled, tests on a number of samples of various materials were made by the two methods. The results of these tests appeared to indicate that the two methods did not give satisfactory agreement. The differences however, were not consistent either in magnitude or sign. A search for the reason for the discrepancies finally led to the conclusion that the cause lay in the behavior of the material rather than in the methods themselves. It was found that if consistent and reproducible results are to be obtained, a certain definite procedure must be followed. If this is done, the results obtained by the two methods on the same sample agree within reasonable limits.

II. TESTING METHODS

The two methods employ alternating current and are designated as the bridge method and the potentiometer method, respectively. The specimen is of the same form for either method and consists of strips of sheet material 25 cm long and 3 cm wide built up in the form of a

[1] ASTM Standards, 404(1933).

square with butt and lap joints at the corners. The strips are inserted in forms upon which there are two uniformly distributed windings of 100 and 1,000 turns, respectively. In the bridge method only one of the coils is used, the choice depending upon the type of material to be tested. In the potentiometer method both coils are used, one as a primary and the other as a secondary.

The bridge is a parallel Owen bridge by which values of self-inductance and apparent resistance of the test winding are determined. The permeability of the specimen is calculated in terms of the measured inductance and the core loss is calculated from the excess of the apparent resistance of the test winding over its ohmic resistance. The maximum induction is proportional to the voltage applied to the bridge and measured with a suitable voltmeter. For tests at 60 cycles per second, a vibration galvanometer is used as a detector.

The potentiometer is of the coordinate type which indicates voltage in terms of two components having a quadrature phase relation. The maximum induction is calculated in terms of the voltage induced in the secondary winding. The phase relations are adjusted so that this voltage is in phase with one of the components of the potentiometer. The two components of the drop across a standard shunt connected in series with the primary winding are then determined. The magnetizing force is calculated in terms of the component in quadrature with the induced voltage and the loss is calculated in terms of the in-phase component taking into consideration the ratio of the number of turns in the two windings. One of the essential conditions for either test is that the applied voltage shall have approximately a sine wave form, with not more than 10 percent of total harmonics present. The range of inductions for which these methods apply is from 10 to 1,000 gausses.

Before making a test by either method, the material is demagnetized with 60-cycle alternating current which is gradually reduced from a value sufficient to bring the material into the third stage of magnetization to a value lower than the lowest to be used in making a measurement. It is not necessary to repeat the demagnetizing process provided that points are taken in the order of increasing values of magnetizing force.

III. OBSERVATIONS AND RESULTS

Tests were made in the range of induction from 10 to 100 gausses on several samples of silicon steel and hipernik. In some cases it appeared that the values of permeability for a given value of maximum induction as determined by the potentiometer were higher than those determined by the bridge method. On the other hand, it was sometimes found that the higher results were obtained by the bridge method. Moreover, check tests by either method seldom agreed with the original results obtained by the same method, the differences sometimes amounting to as much as 10 or 12 percent.

A clue as to the source of the difficulty was found in an article by S. P. Boudrine [2] in which it was stated that the value of permeability obtained depends upon the interval of time which elapses between demagnetization and the test. This phenomenon has also been

[2] Boudrine, Trv. de l'Insu. de Met. et Stand. de l' U.R.S.S., **4**, 77(1933).

noted by Wild and Perrier [3] and by Steinhaus.[4] Its importance with respect to practical magnetic testing has been emphasized by the increasing use of magnetic materials at very low values of induction and by the development of methods of testing materials at low inductions on a routine basis.

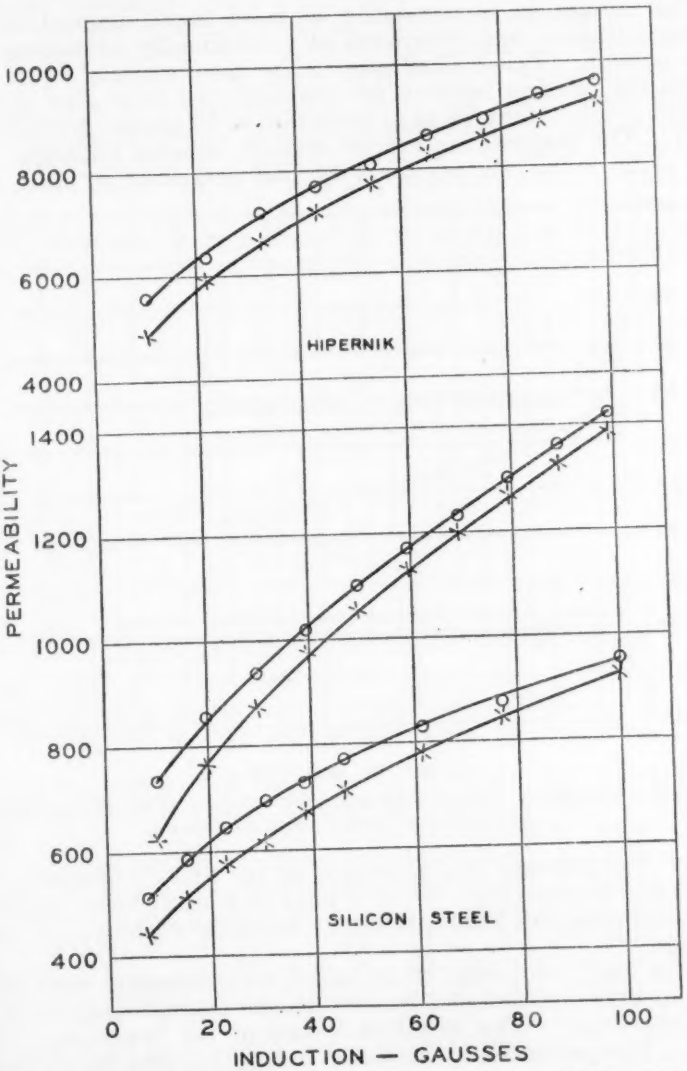

FIGURE 1.—*Showing differences in permeability obtained by testing immediately and 18, 19, or 20 hours after demagnetization.*

Circles represent points obtained immediately and crosses represent points obtained after the lapse of time.

The results obtained with three typical materials will serve to illustrate the phenomenon. Curves for two types of silicon steel and for a sample of hipernik are shown in figure 1. The data for the

[3] Wild and Perrier, Arch. d. Scien. Phys. et. Nat., **7**,209(1926).
[4] Steinhaus, Z. f. Tech. Phys. **7**,492(1926).

upper curves were taken immediately after demagnetization and in as short a time as possible. The lower curves were taken 18, 19, and 20 hours, respectively, after the specimens had been demagnetized. Experiments showed that the results did not depend upon the method of demagnetization.

The change in permeability is most rapid immediately after demagnetization and progresses at a continually decreasing rate as time goes on. This is illustrated in the upper curve of figure 2 which shows the relation between permeability and time after demagnetization at a constant value of induction of 50 gausses for silicon steel no. 1. The magnetizing current was off between readings. At the end of 20 hours the permeability had decreased by 10.4 percent.

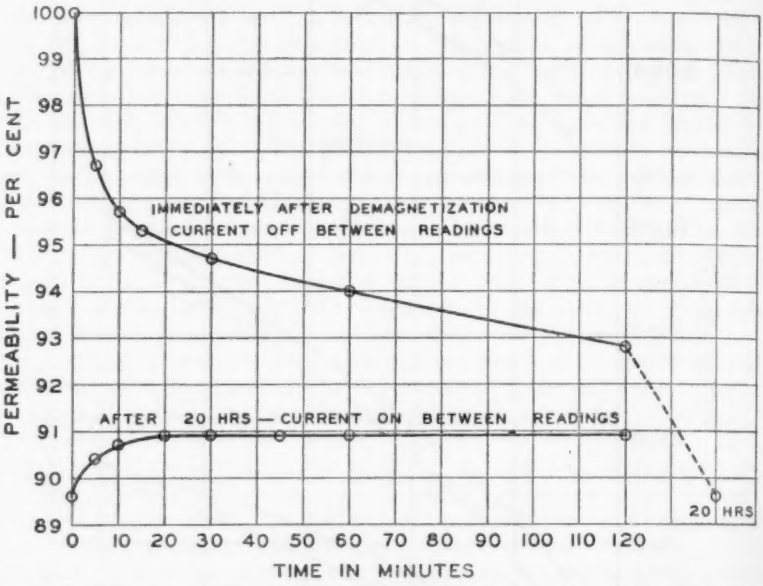

FIGURE 2.—*Change of permeability with time elapsed after demagnetization as observed at an induction of 50 gausses.*

Half of this decrease took place during the first 30 minutes. If the alternating magnetizing current is kept on continuously, the permeability decreases, but less rapidly than when the current is off between readings.

At the end of a period of 20 hours, measurements were made at intervals over a period of 2 hours with the magnetizing current kept on continuously. The result is shown in the lower curve in the figure. The permeability increased during the first 20 minutes and then remained at a constant value. The total change in this instance, however, was only 1.3 percent.

The change in permeability is not associated primarily with alternating-current magnetization. Measurements were made on the same sample of silicon steel by the direct-current ballistic method. The results obtained at a constant magnetizing force of 0.036 oersteds are shown in figure 3. In this case the permeability decreased 12.6

percent in 2 hours. The magnetizing current was on only during the time necessary to make a reading.

Although the primary object of the investigation was to determine how closely the results obtained by the two testing methods on identical samples should be expected to agree and to establish a procedure for obtaining consistent and reproducible results, it may be of interest to consider some of the possible causes of the observed change in permeability. The iron-nickel alloys of which hipernik is an example have a decided tendency to be less stable magnetically than the iron-silicon alloys. It would not have been surprising, therefore, if it had been found difficult to obtain reproducible results with the iron-nickel alloys only. It appears, however, that the phenomenon is just as pronounced in the iron-silicon alloys. It cannot be considered, therefore, to be a characteristic of any particular type of material. Other possible causes which might be considered are mag-

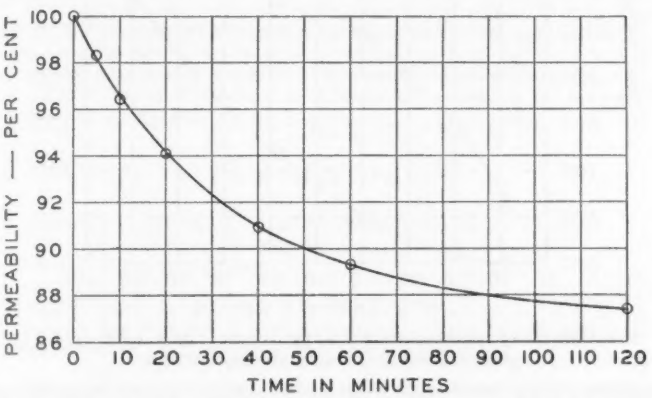

FIGURE 3.—*Change of permeability with time elapsed after demagnetization observed by the ballistic method at a magnetizing force of 0.036 oersteds.*

netic viscosity, aging, and temperature changes. The effect is entirely different from magnetic viscosity and the materials investigated are of the kinds in which viscosity effects are usually not pronounced. Silicon steel is generally considered to be practically nonaging. One of the samples tested is known to have been in the laboratory for at least 20 years, during which time any aging which might take place should be practically complete. Furthermore, since the change is reversible and can be reproduced at will, the phenomenon should not be ascribed to aging effects. Neither should it be ascribed to ordinary temperature effects. The magnitude of the change is much greater than could be accounted for in terms of the temperature coefficient of magnetic permeability.

It might be thought that the phenomenon is related in some way to the influence of the earth's field, which is from 10 to 20 times as great as the magnetizing forces used in the measurements. However, the drift was observed even when the specimen was so oriented as to bring the earth's field at right angles to that of the magnetizing coils.

Although no theoretical explanation of the phenomenon is offered, the immediate and practical objects of the investigation have been

attained. Results reproducible within 1 or 2 percent are satisfactory for ordinary commercial testing. This degree of reproducibility can be obtained by waiting from 18 to 24 hours after demagnetization before making a test. By following this procedure the results shown in figure 4 were obtained. These show that the agreement between the two methods both as to permeability and core loss is within the allowable experimental error.

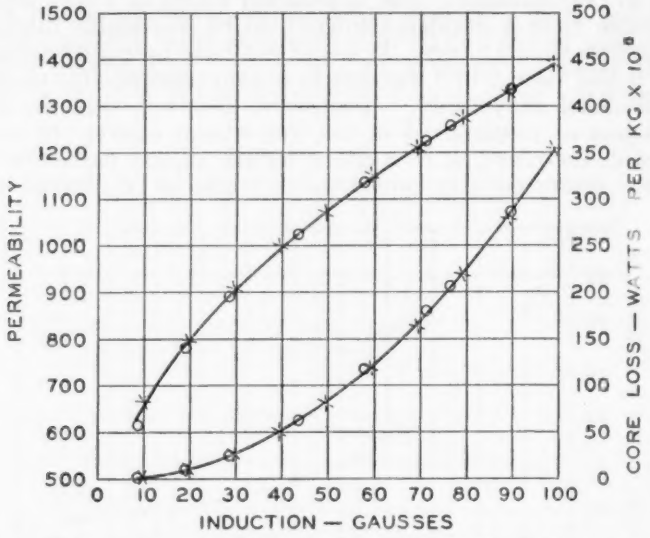

FIGURE 4.—*Values of permeability (upper curve) and core loss (lower curve) obtained 24 hours after demagnetization.*

Circles represent points obtained by the bridge method. Crosses represent values obtained by the potentiometer method.

IV. SUMMARY

Since the standard specifications for magnetic testing recently adopted by the American Society for Testing Materials permit the use of either of two alternative methods for tests at very low inductions, it is important that results obtained on the same sample by the two methods shall be in agreement. Tests carried out for the purpose of determining whether or not this requirement is fulfilled showed an apparent lack of agreement which was finally traced to the behavior of the material rather than to any systematic difference between the two methods. It has been found that at very low inductions the magnetic permeability decreases with time after demagnetization. The rate of change is a maximum immediately after demagnetization and decreases as time goes on. The total change may be of the order of 10 to 15 percent. If a sufficient length of time (18 to 24 hours) is allowed to elapse between demagnetization and testing, it is possible to obtain consistent and reproducible values both of permeability and core loss. When this precaution is taken, values obtained on the same specimen by the two methods permitted by the specifications of the American Society for Testing Materials should be in agreement within the allowable experimental error.

WASHINGTON, June 5, 1934.

U.S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP715

Part of Journal of Research of the National Bureau of Standards, Volume 13, September 1934

CRITICAL STUDY OF THE DETERMINATION OF ETHANE BY EXPLOSION WITH OXYGEN OR AIR

By Joseph R. Branham and Martin Shepherd

ABSTRACT

This paper presents the results of a series of analyses of pure ethane by the explosion method. Explosions were made with commercial oxygen, pure oxygen, and air. The results are compared with previously reported data obtained by slow combustion. Large differences were observed between the various groups of analyses, and no group gave results corresponding to the ideal equations. These differences are partly explained by errors found and measured. In general, the explosion methods were very inaccurate, possibly far more inaccurate than is commonly suspected.

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I. INTRODUCTION AND SUMMARY OF ALL OBSERVED DATA

In a previous study of the determination of ethane by the slow combustion method,[1] it was found that ethane (known to be pure) did not react in accordance with the ideal volumetric equation, $C_2H_6+3.5\ O_2 \rightarrow 2.0\ CO_2+2.5TC$, but gave instead a reaction expressed by the volumetric equation

$$C_2H_6+3.513\ O_2 \rightarrow 1.994\ CO_2+2.520\ TC,$$

where O_2, CO_2, and TC are symbols used to identify the numbers representing the relative volumes of oxygen consumed, carbon dioxide produced, and contraction, respectively, upon burning one volume of ethane. This observed equation does not agree with the ideal equation even when the latter is corrected for the deviations of ethane and carbon dioxide from ideality. Several sources of error inherent to the process were found, such as solution of ethane and carbon dioxide in the distributor connections and lubricant; and when the measured effects of these errors were taken into account, the corrected

[1] Martin Shepherd and Joseph R. Branham, *A critical study of the determination of ethane by combustion over platinum in the presence of excess oxygen.* BS J.Research **11** 783(1933);RP625.

results were in only fair agreement with the observed data, which were thus partially, but not fully, explained.

The present paper reports the results of a similar study of the determination of ethane by the explosion method. The ethane examined was from the same container as that used in obtaining the data by the slow combustion method, and was known to be pure so far as this work is concerned, since the only impurity detected (by the previously reported sensitive method) was approximately 0.01 percent of nitrogen.[2] This ethane was burned explosively with oxygen from three sources:

(1) Commercial oxygen obtained by air separation, containing 0.76 percent of nitrogen (or nitrogen + inerts).

(2) Pure oxygen, obtained electrolytically (from sodium hydroxide), from which hydrogen was removed by repeated passage over a glowing platinum spiral. In this case, it is also important to note that pure oxygen replaced the nitrogen ordinarily employed to fill the distributor and the manometer arm connected thereto. Thus any effect caused by the presence of nitrogen was eliminated.

(3) Oxygen in normal air.

The three series of analyses employing oxygen from the sources mentioned gave different results, and all these results differed from those obtained by slow combustion. The following volumetric relationships represent the averages taken from the observed data, and illustrate this divergence.

(1) Explosion with commercial oxygen:

$$C_2H_6 + 3.558\ O_2 \rightarrow 1.986\ CO_2 + 2.594\ TC.$$

(2) Explosion with pure oxygen:

$$C_2H_6 + 3.525\ O_2 \rightarrow 1.988\ CO_2 + 2.525\ TC.$$

(3) Explosion with air:

$$C_2H_6 + 3.497\ O_2 \rightarrow 1.990\ CO_2 + 2.528\ TC.$$

For comparison, the observed result for slow combustion[3] may again be given:

$$C_2H_6 + 3.513\ O_2 \rightarrow 1.994\ CO_2 + 2.520\ TC.$$

The results observed are also presented graphically (fig. 1) as percentages of ethane computed from the observed analytical data. (These results are computed from equations given in fig. 1, wherein S represents the volume of sample.) The deviations from 100 percent at once establish the relative accuracy of the various methods. The precision (i.e., reproducibility of results) of the methods is also apparent from the scattering of points. The results for the 18 analyses by slow combustion, taken from the previous report, are included for comparison. The data obtained by each of the four methods are grouped separately, and the results obtained by each method of computation are represented by a separate symbol. Where

[2] The determination of the purity of the ethane used in the present work is given in the previous report (see footnote 1). A detailed description of the method used for this test is given in BS J.Research 11, 185(1934); RP643.

[3] See footnote 1.

identical numerical results were obtained, they were plotted one above another on the same vertical line.

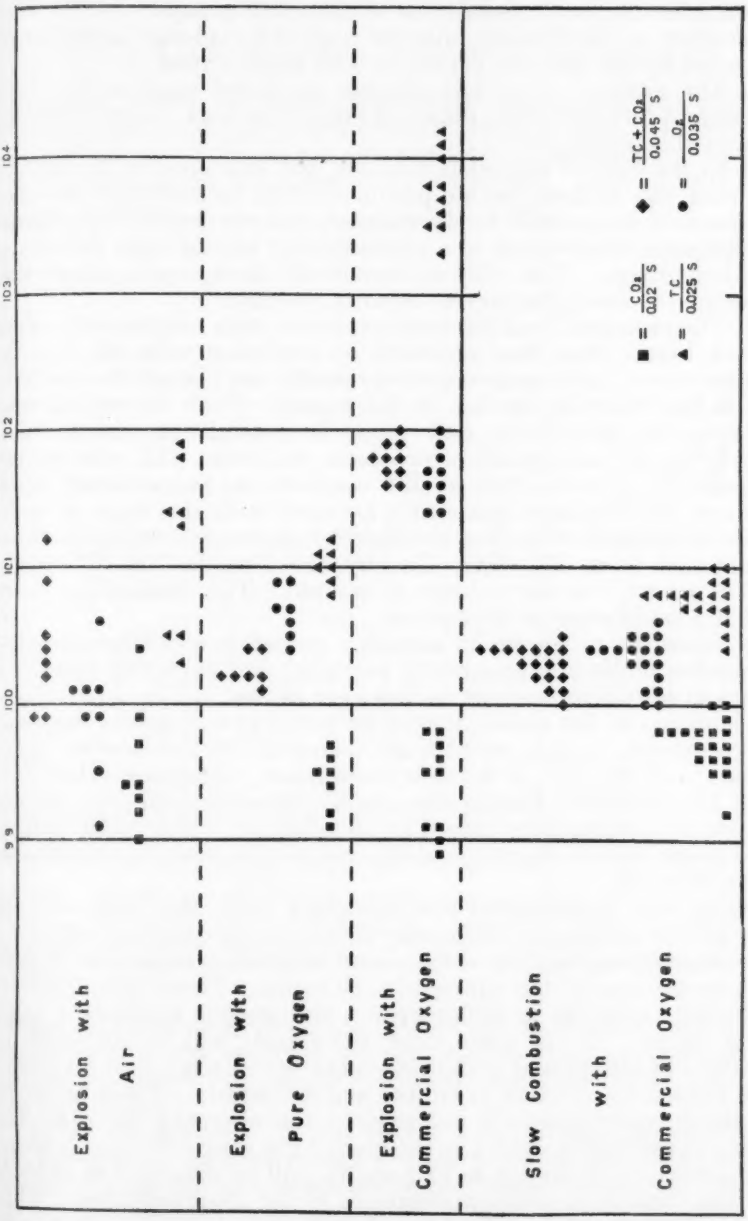

FIGURE 1.—*Results of the determination of pure ethane by explosion with commercial oxygen, pure oxygen, and air.* Previously reported data for slow combustion are included. The commercial oxygen was obtained by air separation and contained about 0.7 percent of nitrogen. In the analyses with pure oxygen, nitrogen was eliminated from the reaction.

A brief survey of the observed results (fig. 1) and of the average volumetric equations given will at once indicate several important facts.

(1) It is apparent that the presence of small amounts of nitrogen during the explosion will greatly influence the contraction and oxygen consumed. The values in the case of explosion with commercial oxygen differ markedly from those of the other groups.

The effect of eliminating nitrogen from the explosion is strikingly illustrated by the data for explosion with pure oxygen.

(2) The amount of carbon dioxide produced exhibits the least tendency to differ between different groups; indeed, these values are in reasonable agreement.

(3) In the case of explosion with air, the averages for the oxygen consumed and carbon dioxide produced seem to indicate a satisfactory reaction, but, as will be shown later, this group afforded evidence of incomplete combustion to a much greater extent than did any of the other groups. The wide divergence of these results shows that the method is unsatisfactory as regards precision.

(4) The precision resulting from explosion with commercial oxygen is much better than that obtained by explosion with air, but the accuracy is extremely poor unless the results are corrected (as will be done in the following section of the paper). Such corrections may not always be satisfactory, and cannot be generally recommended.

(5) From the standpoint of precision, explosion with pure oxygen is apparently as satisfactory as slow combustion; the accuracy is not. However, the accuracy apparently attained with this type of explosion is comparable with that obtained by slow combustion, if ethane is computed from $TC+CO_2$ (i.e., by the formula $100\ (TC+CO_2) \div 4.5\ S$, where S is the volume of sample. The method has some merit if a rapid analysis is required.

(6) From the viewpoint of accuracy as well as precision, the slow combustion method is apparently superior; but even this method is subject to considerable error, as has been shown.

In addition to the above, it may be noted in the case of explosion with commercial oxygen or with air, nitrogen was lost in every single analysis.[4] In the case of the slow combustion, nitrogen was lost in 13 out of 18 analyses.[4] But in the case of explosion with pure oxygen, nitrogen was apparently gained in all analyses. This point is illustrated graphically in figure 2, but discussion of its probable significance will be deferred.

Having thus summarized the important facts, the balance of the paper will be devoted to discussing the observed data for each of the series of analyses, together with several interesting experimental facts which were found in the course of each series. These facts illustrate peculiarities inherent in the processes, and suggest methods of minimizing errors. At the same time, the results will be corrected for deviations of ethane and carbon dioxide from ideality, and for known errors caused by solution in rubber and lubricant. It will be shown that these corrections will not explain the observed facts, as they did to a considerable extent in the case of the slow combustion series. Other errors, some known to be present, will be discussed in order to show the various possible explanations of the observed data. While these are worth noting, the analyst will find that his real interest must center in the fact that the accuracy which can be obtained by any of these methods is very far from satisfactory, perhaps farther

[4] The figure shows several points on the O ml line. This happens simply because the data actually obtained are given to the nearest 0.02 ml.

than is generally suspected. Thus, employing the commonly used method of computation,[5] it is possible to obtain indications of 12 to 18 percent of methane (where it is known there is no methane) and about 90 percent of ethane, for a round sum of 106 to 108 percent of sample.

II. EXPLOSION WITH COMMERCIAL OXYGEN

As stated before, the commercial oxygen was obtained by air separation and contained 0.76 percent of nitrogen and inerts. In addition, the distributor and the distributor arm of the manometer were filled with nitrogen at the beginning of each analysis. Thus 2 to 3 ml of

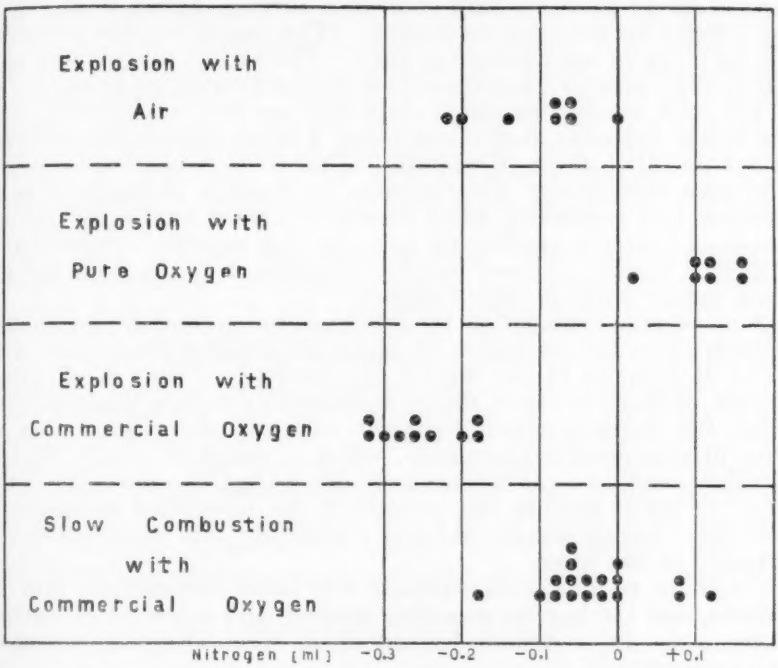

FIGURE 2.—*"Nitrogen" lost or gained during each analysis by the various methods.*

This "nitrogen" represents the failure to check the original amount of gas present in the distributor and manometer at the beginning of each analysis. Since there was no nitrogen in the sample of ethane, the "nitrogen" observed may represent volumetric error or gas which did not react during combustion or absorption.

nitrogen was present at the time of the explosion of the ethane-oxygen mixture, and it was expected that some of the nitrogen would react with the oxygen, which was always in excess of that required to react with the ethane.

The analytical procedure was simple. After filling the distributor with nitrogen at the fixed pressure of the compensator, an average of 10.6 ml of pure ethane was measured and transferred to an explosion pipette. (This pipette was constructed with very heavy walls, and with no stopcock at the bottom to restrict surges of mercury. The spark gap was arranged so that the spark might be passed at the dome or at the center of the pipette.) The sampling lines were then care-

[5] Methane and ethane computed from TC and CO_2 according to the conventional equations.

fully flushed with mercury and with oxygen, following which an average of 62.8 ml of the commercial oxygen was measured and transferred to the explosion pipette. This oxygen (together with the gas in the manometer) was passed rather slowly through the distributor, so that ethane which had dissolved in the rubber and lubricant might have opportunity to be regained (at least partially) and so be carried into the explosion pipette. The gases were throughly mixed in the explosion pipette, and then ignited under slightly reduced pressure. The explosion was violent. Following the explosion, the residual gas was (1) returned to the burette where measurements were taken over a period of 10 to 15 minutes; or (2) allowed to remain in the explosion pipette for 10 minutes, with occasional stirring, before returning to the burette for final measurements. (The reason for this technique will be given in the next paragraph.) The carbon dioxide was then removed by ascarite,[6] and the excess oxygen by alkaline pyrogallol.

The most notable feature of these analyses was the fact that after the actual explosion had taken place, a small contraction occurred over a period of about 10 minutes. Thus if the products of combustion were immediately transferred to the burette, it was possible to measure this continuing small contraction until finally the volume remained constant (within .02 ml). In this manner, several tenths of one ml would disappear between approximately the third and the tenth minute elapsing after explosion.[7]

A reasonable explanation for this observed secondary contraction appears to be the formation of oxides of nitrogen which react with water or mercury in the pipette and burette. (Solution of carbon dioxide, or thermal effects, do not satisfactorily explain this behavior.) Thus, the nitrogen which combines with excess oxygen causes an error of considerable magnitude, which is reflected in the TC and O_2 values, and does not substantially affect the CO_2, since little if any NO_2 (or N_2O_4) reaches the ascarite if the prescribed technique is followed. Experimental evidence supporting this explanation was obtained in two ways.

(1) If the residue from explosion was taken immediately into the burette, and the burette was then washed with a few ml of distilled water, a cloudy precipitate formed which, when analyzed, proved to be a mercury salt.

(2) The explosion pipette was washed with 10 ml of distilled water and 20 ml of nitrate-free sulphuric acid (95 percent), and the solution tested for nitrates by adding 0.5 ml of saturated ferrous sulphate solution. A strongly positive test for nitrates was obtained.

This explanation also agrees with the fact that nitrogen was lost in every one of the 10 analyses of this series. This loss averaged 0.25 ml with no great deviation therefrom, and is illustrated graphically in figure 2.

Determinations of carbon monoxide occurring in the products of combustion were made for several analyses of each group.[8] These

[6] For details of this procedure for the removal of carbon dioxide, see previous report, footnote 1.

[7] This behavior was observed by the second author in 1919–21 in connection with the explosion of natural gas with oxygen. A study of the error involved in the analysis of natural gas from the Petrolia, Tex., field indicated average errors of several percent. In this work, the residual contraction measured over the first 3 minutes following the explosion was usually over 0.3 ml. (Unpublished report of the U.S. Experimental Helium Plant no. 3, by Martin Shepherd and F. W. Schraeder).

[8] Carbon monoxide was determined by the iodine pentoxide method. These determinations were made by Carroll Creitz of this laboratory.

determinations furnished one of two series of experimental data used to judge the completeness of combustion. For the explosions with commercial oxygen, an average of 0.03 ml of CO was found in the products of combustion, corresponding roughly to 0.3 percent of the average volume of the sample used.

The second experimental evidence used to judge the completeness of combustion was obtained by burning the residue from the explosion (after first removing the carbon dioxide) by passage over the heated platinum spiral of the combustion pipette. Whenever this was done a slight additional contraction was observed, and some additional carbon dioxide found. The amounts involved were small—of the order of magnitude of 0.1 to 0.3 ml for the sum of the additional $TC+CO_2$. The significance of these observations is uncertain, not only because of the small volumes involved (which would represent, of course, much smaller volumes of C_2H_6), but also because of the fact that, if unburned C_2H_6 was really found, it may have come from the rubber and lubricant of the distributor rather than from the products of explosion. Hence, this evidence tends only to throw suspicion upon the completeness of combustion, rather than to prove it quantitatively.

With these various experimental facts and the corresponding possible explanations in mind, it will be interesting to examine the observed data merely to see what might have happened to produce these results. For this purpose, only the average results will be employed. They will first be corrected for errors known to be present, and finally for errors which may or may not have been present.

Since ethane was the only combustible compound present, the amount can be computed from the observed TC, CO_2 or O_2 (or various combinations of these quantities). If the ideal volumetric relationships prevail, all methods of calculation should give an identical result; and with the ethane used, the common result would be 100 percent. In the following computations, ethane will be computed from the three relevant quantities, according to the equations:

$$(1)\quad \text{Percent } C_2H_6 = TC/2.5\ S \times 100$$

$$(2)\quad \text{Percent } C_2H_6 = CO_2/2.0\ S \times 100$$

$$(3)\quad \text{Percent } C_2H_6 = O_2/3.5\ S \times 100$$

In addition a formula which has the merit of automatically correcting for deviations of carbon dioxide from ideality, and losses of carbon dioxide by solution in rubber, lubricant and water will be occasionally included:

$$(4)\quad \text{Percent } C_2H_6 = (TC+CO_2)/4.5\ S \times 100$$

The object of the computations will be to show the effect of known errors, by correcting the observed data; and then to show how closely these corrected data may be made to agree (1) among themselves and (2) with the known purity of the sample.

The average percentages of ethane computed from the various observed data for this series of explosions are: from TC, 103.8; from CO_2, 99.3; from O_2, 101.7; (from $TC+CO_2$, 101.8).

The first corrections to be applied are (1) for the deviations of ethane and carbon dioxide from ideality, and (2) for the known losses of ethane and carbon dixoxide by solution. These corrections are made in exactly the same manner as in the previous report covering the analysis by slow combustion.[9] The only differences are (a) the factor used for deviation of carbon dioxide was slightly changed to correspond to the lower average partial pressure of this gas in the products of combustion; and (b) a smaller correction was made for losses by solution, since the procedure for explosions required less time. When these corrections are made, the percentages of ethane become: from TC, 103.0; from CO_2, 98.7; from O_2, 100.7; (from TC+CO_2=101.1). Such corrections are not sufficient to bring the various quantities into agreement with themselves or the known sample.

Next, a correction can be made for the average amount of carbon monoxide found. If this is done, the results are only slightly altered. The percentages of ethane are: from TC, 103.1; from CO_2, 98.9; from O_2, 100.8.

Following this correction, one can be made for the measured loss (0.25 ml) of nitrogen. An assumption (which seems reasonably verified by experimental evidence) must be made—i.e., that the nitrogen lost combined with oxygen to form N_2O_4, which reacted with water or mercury and disappeared from the gas phase before the absorption of carbon dixoide. Corrections made according to these assumptions change the calculated percentages of ethane to the following values: from TC, 99.9; from CO_2, 98.9; from O_2, 99.3.

It may now be interesting to make several additional assumptions regarding the possible degree of incompleteness of combustion, although little experimental evidence is at present available to support them. Aside from the determination of carbon monoxide in the products of combustion, and the doubtful evidence presented by the small secondary TC+CO_2 produced when the products of explosion were burned by the slow combustion method, there is some additional information which tends to throw suspicion on the completeness of combustion. This information did not appear until the series of explosions with pure oxygen, and it is therefore necessary at this point to anticipate. Referring to figure 2, which illustrates graphically the amount of gas left at the end of each analysis (which is ordinarily called nitrogen or inert, but which really represents the amount by which the analysis failed to reach the original balanced condition of the nitrogen-filled distributor system), it will be seen that "nitrogen" was lost in the great majority of cases, but was invariably gained in the series of explosions with pure oxygen. Since there was no measurable amount of nitrogen in the sample nor in the oxygen, this apparent gain of nitrogen must have been caused by (1) leakage from the outside, (2) solution of nitrogen (from the outside air) in the rubber connections and subsequent diffusion through the tubing, (3) the incomplete absorption of carbon dioxide or oxygen, (4) nitrogen given off from the reagents used to absorb these two gases, or (5) the actual presence of a portion of the original sample in some form or forms of incomplete combustion. Examining the likelihood of these possibilities in the order given: (1) Freedom from actual leakage was insured by repeated tests; (2) the time required for an analysis, together with the known permeability of rubber to nitrogen, throws doubt upon the

[9] See footnote 1.

possibility of gaining 0.1 ml of nitrogen through the rubber, although this is not altogether impossible; (3) repeated tests have established the completeness of absorption with the technique employed; (4) the reagents used were in substantial equilibrium with nitrogen at the beginning of the analyses, with no great changes in pressure or temperature to alter this condition. This indicates that there might have been some ethane not completely burned at the end of the analyses.

If we assume this to be so, there are two corrections to be applied in consequence. The first of these follows from the fact that the measured nitrogen lost during the explosions with commercial oxygen is in all probability too low by the amount of the "nitrogen" gained during the explosions with pure oxygen. The second correction comes from the fact that apparently 0.1 ml of C_2H_6 did not completely burn. Since only 0.03 ml of carbon monoxide appeared in the products of combustion, it does not seem entirely unreasonable to suppose that the greater portion of the remainder still existed as ethane. (This, of course, is not necessarily true. But if other intermediate products are assumed, the corrections become hopeless, and in order to make any at all, the above assumption must be accepted.) Making these two corrections, the results (percentages of ethane) become: From TC, 99.8; CO_2, 99.5; O_2, 99.6.

Another viewpoint of the subject of incompleteness of combustion is afforded by comparing the carbon dioxide produced in each group of analyses. It will be seen (fig. 1) that these values are in fairly good agreement in every case, and apparently do not show the divergence exhibited by the contraction and oxygen consumed. It is somewhat gratifying to observe that if the carbon dioxide produced is taken as the measure of the completeness of combustion, and the data are corrected on this basis (including as before a correction for the additional nitrogen burned), the results are in reasonable agreement with those previously obtained on the basis of "nitrogen" gained. The percentages of ethane are: From TC, 99.7; from CO_2, 100.0 (by definition); from O_2, 99.8.

However, too much significance should not be accorded the assumption that the carbon dioxide correctly measures the completeness of combustion, especially in view of the fact that the carbon dioxide did not indicate the relative incompleteness of the explosions with air.

While these conjectures are somewhat interesting, the analyst should not lose sight of the really significant fact that the accuracy is far from satisfactory whatever the nature of the errors may be.

III. EXPLOSION WITH PURE OXYGEN

This group of analyses present a relatively simple picture, devoid of many of the complications encountered in the preceding group. The analysis of the data is correspondingly straightforward.

The analytical procedure was essentially the same as that used for the explosions with commercial oxygen, except that pure oxygen, instead of nitrogen, was used to fill the distributor (and the arm of the manometer attached thereto) at the beginning of each analysis. Thus nitrogen was eliminated from the reaction. This technique was made possible by the use of the calibrated distributor and manometer previously described.[10]

[10] For a detailed description of the use of the calibrated distributor, consult BS J. Research **6**, 121(1931); RP266.

The result of eliminating nitrogen is shown by the sharp change in the values calculated from TC and O_2 values (see fig. 1). Indeed, these values are shifted to agree substantially with those obtained by the slow combustion method. It is worthy of note that the continued contraction after explosion, observed when commercial oxygen was used, was not detected in the present series.

The average observed data, calculated as percentages of ethane, give the following results: From TC, 101.0; from CO_2, 99.4; from O_2, 100.7.

When these data are corrected (in the same manner as before) for the deviations of ethane and carbon dioxide from ideality, and for the known losses of ethane and carbon dioxide by solution, the results are: from TC, 100.2; from CO_2, 98.8; from O_2, 99.8.

These results, corrected in turn for the measured carbon monoxide found in the products of combustion, become: from TC, 100.3; from CO_2, 99.0; from O_2, 99.9.

If it is now assumed that the measured gain of nitrogen represents a corresponding amount of unburned sample which exists as ethane, the corrected data become: from TC, 101.1; from CO_2, 99.7; from O_2, 100.6.

Similarly, if the carbon dioxide produced is accepted as a measure of the completeness of combustion, the corrected data become: from TC, 101.4; from CO_2, 100.0 (by definition); from O_2, 100.9.

Since no nitrogen was present to react with oxygen, with secondary reactions of these oxides with mercury or water, no further corrections need be made.

IV. EXPLOSION WITH AIR

The precision of this series of analyses was discouraging. Apparently the explosions were "not sure of themselves", and were not quantitatively reproducible. The amounts of carbon monoxide found in the products of combustion varied from 0.02 to 0.15 ml, which is additional evidence of the haphazard behavior of such explosions. The amount of sample used was necessarily small (about 5 ml), and the effect of errors of measurement was correspondingly large. Since the method was found so unsatisfactory with regard to precision, it does not seem worth while to discuss any detailed analysis of the errors involved in this case.

However, the results of applying corrections to this group of data are given in figure 3, which affords a graphical representation of the average observed and corrected data for all of the groups of analyses, including the previously reported data for slow combustion. In this figure, the corrections are numbered as follows:

1—Correction for the deviation of ethane and carbon dioxide from ideality.

2—Correction for the loss of ethane and carbon dioxide by solution in the distributor and buret.

3—Correction for carbon monoxide in the products of combustion.

4—Correction for the loss of nitrogen by oxidation.

5—Correction for the additional loss of nitrogen and for the unburned sample, assuming the gain of nitrogen observed during explosions with pure oxygen to be a measure of unburned sample.

6—Correction for unburned sample, assuming CO_2 to be a correct measure of sample burned. (Percentage of ethane calculated from $CO_2 = 100$ by definition. This should be kept in mind when referring to the figure.)

V. THE "RAPID" SLOW COMBUSTION OF ETHANE

It is worth while noting that a period of 2 to 3 minutes is usually specified in the literature as representing the normal duration of a slow combustion. In the previous report [11] it was stated that a much longer period was usually required, in order to insure the

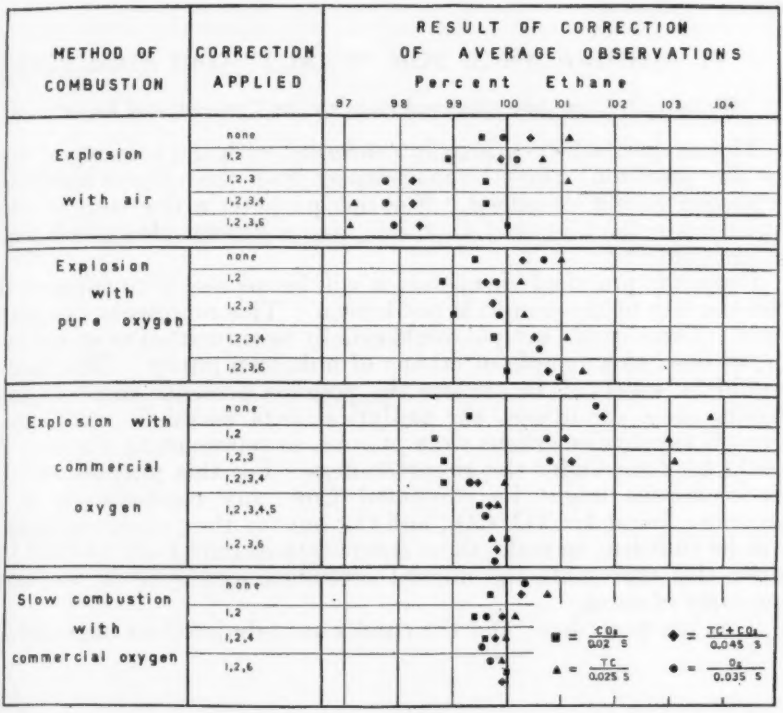

FIGURE 3.—*Analysis of pure ethane by the various methods, reported as the average value obtained for each series, and corrected for both known and assumed errors.*

presence of an excess of oxygen by diffusion around the platinum spiral; and that 30 minutes was usually required to burn ethane satisfactorily.

When a slow combustion is forced to take place within the short period generally prescribed, the reaction does not occur as a true surface conbustion, but instead proceeds as a series of explosions of varying magnitude. Such an analysis might, therefore, be expected to give results intermediate between those obtained by a true slow combustion and an actual explosion.

In order to ascertain whether the "rapid" slow combustion would more nearly approximate the reaction obtained by slow combustion

[11] See footnote 1.

or by explosion (and, at the same time, in the effort to determine the practicability of the conventional procedure), several attempts were made to burn ethane by slow combustion within the allotted 2 to 3 minutes. The most successful of these attempts, from the viewpoint of speed, was accomplished in 4 minutes 25 seconds; while others were somewhat more prolonged (8 minutes). The behavior of the reaction provided a considerable amount of stimulation to the analyst, since at no time was it entirely certain that disaster would be avoided. As was expected, the general tendency was for these combustions to yield results near those found by employing actual explosion—the more rapid the slow combustion, the nearer the answer obtained by direct explosion.

VI. SIGNIFICANCE FOR "EXACT" GAS ANALYSIS

(Results of Computing Observed Data by the Conventional Equations)

The analyst will be primarily concerned with the accuracy (as well as the precision) which he may expect from the various methods of explosion herein described. For this purpose, a few computations, based upon the observed data, will give a general idea of what may be encountered.

From the practical viewpoint, it will be necessary to suppose that the identity of the sample is not known. This represents the normal case. Thus, such a sample would usually be submitted as an unknown or, at best, as a sample of ethane of unknown purity. The analysis would be expected to disclose the possible presence of other gases. Under these conditions, the analytical data would be computed as though two hydrocarbons were present, as representing the best that could be done under the circumstances. For this purpose, the two hydrocarbons might be computed from any combination of the amounts found for TC, CO_2, and O_2; but for the present purpose, it will be sufficient to make these computations only from TC and CO_2, since this represents the normal procedure employed in by far the majority of cases.

This has been done, and the results are tabulated on page 389.

ANALYSIS OF PURE ETHANE

The Observed Data Computed as Percentages of Methane and Ethane from the Contraction and Carbon Dioxide Produced

These results are the ones that would have been obtained by an analyst using the conventional procedures for so-called "exact" gas analysis.

Method		Percentage of methane	Percentage of ethane
Explosion with commercial oxygen.	Range	17.7 12.3	90.0 93.7
	Average of 10 analyses.	14.9	91.9
Explosion with pure oxygen.	Range	6.6 4.3	95.8 97.5
	Average of 8 analyses.	5.4	96.6
Explosion with air	Range	7.7 2.2	95.2 98.9
	Average of 7 analyses.	6.0	96.8

WASHINGTON, June 26, 1934.

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COIL ARRANGEMENTS FOR PRODUCING A UNIFORM MAGNETIC FIELD

By Forest K. Harris

ABSTRACT

A simple method is described for constructing coils which will give a magnetic field that is nearly uniform in magnitude and direction throughout a long cylindrical volume. A study is made of three types of coils and in each case formulas permitting the computation of the field are developed. Data are given showing the departure of the field from uniformity in specific cases and a procedure is outlined for the design of such coils.

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I. INTRODUCTION

The application of electron beams to physical measurements often makes it desirable that the beam shall not be deflected by the earth's magnetic field. In cases where the beam direction cannot be made coincident with the direction of the local magnetic field, the neutralization of the component of the local field perpendicular to the direction of the beam is required. This is especially the case with low-voltage beams, which suffer relatively large deflection even in weak magnetic fields. In order that this neutralization may be accomplished, it is necessary to set up a magnetic field which will be quite uniform in magnitude and direction throughout the long, narrow cylinder which comprises the path of the beam and in such a direction as to compensate the local field tending to deflect the beam.

Such a field may be set up between a pair of plane rectangular coils whose long dimension is parallel to the path of the beam and whose length is somewhat greater than the distance over which compensation is desired. A modification of such a coil system which resulted in a considerable improvement in the uniformity of the

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compensating field has been described by Beyerle[1] and has been briefly discussed by the author,[2] who has used it to compensate the horizontal component of the local magnetic field along the electron-beam path of a cathode-ray oscillograph.

In the present paper it is proposed to give a more complete analysis of the field near the axis of such coils and to show that certain further modifications in the shape of the compensating coils will result in a considerable gain in uniformity of the field.

II. MAGNETIC FIELD OF COMPENSATING COILS

1. GENERAL CONSIDERATIONS

The magnetic field produced at any point in space by an element of a linear conductor carrying current is given by Ampere's law which is conveniently expressed in vector notation as

$$dH/I = [dl,\rho]/\rho^3$$

where dl is the vector circuit element whose sense is that of the current I, and ρ is the vector distance from the circuit element to the point at which the field is to be determined.

For the straight section of wire of length (a, b) shown in figure 1 the field at a point P, distant ρ_0 from the wire, is given by

$$H/I = \mathbf{i}(o) + \mathbf{j}(o) + \mathbf{k}\int_{-b}^{a} \frac{\rho_0 dl}{(\rho_0^2 + l^2)^{\frac{3}{2}}}$$

$$= \mathbf{k}\frac{1}{\rho_0}\left[\frac{a}{(\rho_0^2 + a^2)^{\frac{1}{2}}} + \frac{b}{(\rho_0^2 + b^2)^{\frac{1}{2}}}\right] \qquad (1)$$

where $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$ are unit vectors along the coordinate axes. The field H at the point P is perpendicular to the plane of the paper and toward the reader.

In the discussion which follows, a number of coil shapes, differing from the coils shown in figure 2 solely in the shape of the short end portions, will be considered. For convenience, these several shapes will each be designated by the shape of its end portion, or head. For example, the plane rectangular coils of figure 2 will be referred to as a straight-head coil pair. Although the coils may, and usually will, consist of a number of turns forming a compact bundle, their fields in the region considered will be represented with all necessary accuracy by the formulas here developed for single turns formed of linear elements.

2. STRAIGHT-HEAD COILS

Since the straight-head coils of figure 2 are made up entirely of straight sections an expression for the field at any point can be immediately written from equation 1, as the resultant of the field due to each of the 8 straight sections which form the coil pair.

We will use as a reference line the vertical axis equidistant from each of the 4 vertical coil sides. The field at a point distant (x_1, y_1)

[1] Beyerle, Arch. f. Elektrot., 25,269(1931).
[2] F. K. Harris, BS J.Research 12,87(1934).

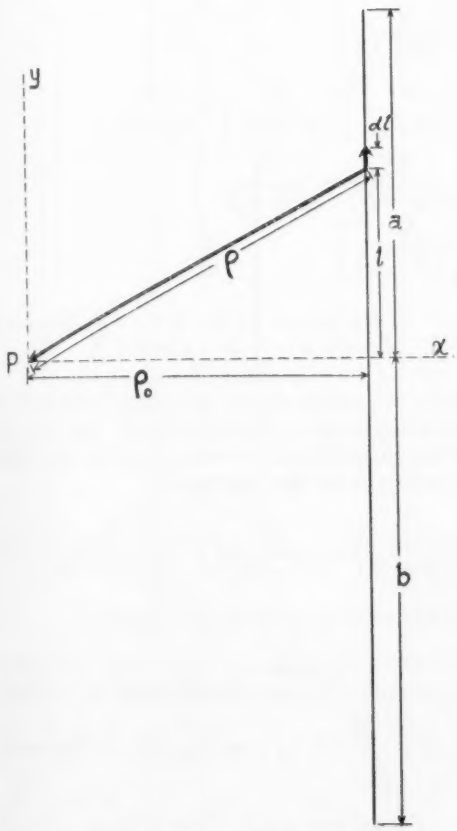

FIGURE 1.

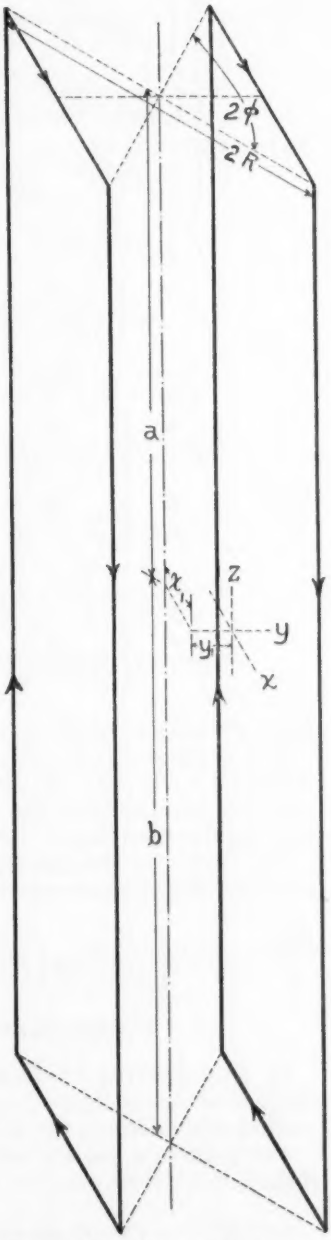

FIGURE 2.—*Straight-head coils.*

from this axis and distant (a, b) from the upper and lower coil heads is given by the expressions

$$\left.\begin{aligned}
\frac{RH_x}{I} &= -\frac{K}{A}\left[\frac{c}{\sqrt{(c^2+A)}}+\frac{d}{\sqrt{(d^2+A)}}\right]+\frac{K}{B}\left[\frac{c}{\sqrt{(c^2+B)}}+\frac{d}{\sqrt{(d^2+B)}}\right]\\
&\quad+\frac{L}{C}\left[\frac{c}{\sqrt{(c^2+C)}}+\frac{d}{\sqrt{(d^2+C)}}\right]-\frac{L}{D}\left[\frac{c}{\sqrt{(c^2+D)}}+\frac{d}{\sqrt{(d^2+D)}}\right]\\
\frac{RH_y}{I} &= \frac{M}{A}\left[\frac{c}{\sqrt{(c^2+A)}}+\frac{d}{\sqrt{(d^2+A)}}\right]+\frac{N}{B}\left[\frac{c}{\sqrt{(c^2+B)}}+\frac{d}{\sqrt{(d^2+B)}}\right]\\
&\quad+\frac{M}{C}\left[\frac{c}{\sqrt{(c^2+C)}}+\frac{d}{\sqrt{(d^2+C)}}\right]+\frac{N}{D}\left[\frac{c}{\sqrt{(c^2+D)}}+\frac{d}{\sqrt{(d^2+D)}}\right]\\
&\quad+\frac{c}{c^2+K^2}\left[\frac{M}{\sqrt{(c^2+A)}}+\frac{N}{\sqrt{(c^2+B)}}\right]+\frac{d}{d^2+K^2}\left[\frac{M}{\sqrt{(d^2+A)}}\right.\\
&\quad\left.+\frac{N}{\sqrt{(d^2+B)}}\right]+\frac{c}{c^2+L^2}\left[\frac{M}{\sqrt{(c^2+C)}}+\frac{N}{\sqrt{(c^2+D)}}\right]\\
&\quad+\frac{d}{d^2+L^2}\left[\frac{M}{\sqrt{(d^2+C)}}+\frac{N}{\sqrt{(d^2+D)}}\right]\\
\frac{RH_z}{I} &= -\frac{K}{c^2+K^2}\left[\frac{M}{\sqrt{(c^2+A)}}+\frac{N}{\sqrt{(c^2+B)}}\right]+\frac{K}{d^2+K^2}\left[\frac{M}{\sqrt{(d^2+A)}}\right.\\
&\quad\left.+\frac{N}{\sqrt{(d^2+B)}}\right]+\frac{L}{c^2+L^2}\left[\frac{M}{\sqrt{(c^2+C)}}+\frac{N}{\sqrt{(c^2+D)}}\right]\\
&\quad-\frac{d}{d^2+L^2}\left[\frac{M}{\sqrt{(d^2+C)}}+\frac{N}{\sqrt{(d^2+D)}}\right]
\end{aligned}\right\} \quad (2)$$

Here $c=a/R$; $d=b/R$; $A=h-s-t$; $B=h+s-t$; $C=h-s+t$; $D=h+s+t$; $K=\cos\phi-g$; $L=\cos\phi+g$; $M=\sin\phi-f$; $N=\sin\phi+f$, where $f=x_1/R$; $g=y_1/R$; $h=1+f^2+g^2$; $s=2f\sin\phi$; $t=2g\cos\phi$. R is the distance from the axis to the vertical coil sides and ϕ is half of the angular opening of the coil sides as seen from the axis (see fig. 2).

For points on the axis the x-component and z-component of the field are zero and the y-component reduces to the expression

$$\frac{RH_y}{I}=4\sin\phi\left[\frac{c}{\sqrt{(1+c^2)}}\left(1+\frac{1}{c^2+\cos^2\phi}\right)+\frac{d}{\sqrt{(1+d^2)}}\left(1+\frac{1}{d^2+\cos^2\phi}\right)\right] \quad (3)$$

3. CIRCULAR-HEAD COILS (FIELD AT AXIS)

If, as suggested by Beyerle, the coil ends be bent into arcs of a circle as shown in figure 3 we must solve Ampere's equation for a circuit section which forms the arc of a circle.

For points on the axis we have for the field resulting from the upper right-hand circuit section

$$\begin{aligned}
\frac{H}{I} &= -\mathbf{i}\int_{-\phi_1}^{\phi_1}\frac{aR\sin\phi d\phi}{[a^2+R^2]^{\frac{3}{2}}}+\mathbf{j}\int_{-\phi_1}^{\phi_1}\frac{aR\cos\phi d\phi}{[a^2+R^2]^{\frac{3}{2}}}-\mathbf{k}\int_{-\phi_1}^{\phi_1}\frac{R^2 d\phi}{[a^2+R^2]^{\frac{3}{2}}}\\
&=\mathbf{i}(o)+\mathbf{j}\frac{2aR\sin\phi_1}{[a^2+R^2]^{\frac{3}{2}}}-\mathbf{k}\frac{2R^2\phi_1}{[a^2+R^2]^{\frac{3}{2}}}
\end{aligned} \quad (4)$$

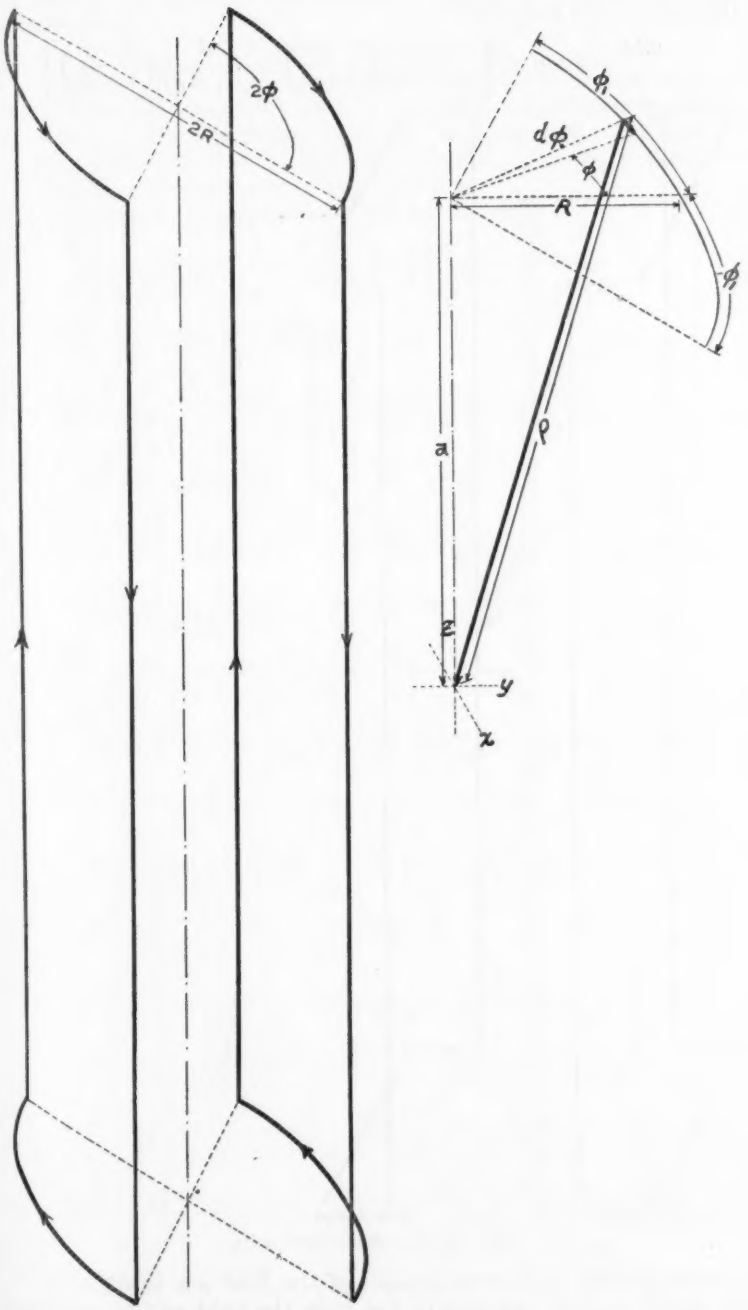

FIGURE 3.—*Circular-head coils.*

By using equations 1 and 4 we can write an expression for the field at the axis of the coil pair

$$\frac{RH_y}{I}=4\sin\phi_1\left[\frac{c}{\sqrt{(1+c^2)}}\left(\frac{2+c^2}{1+c^2}\right)+\frac{d}{\sqrt{(1+d^2)}}\left(\frac{2+d^2}{1+d^2}\right)\right] \quad (5)$$

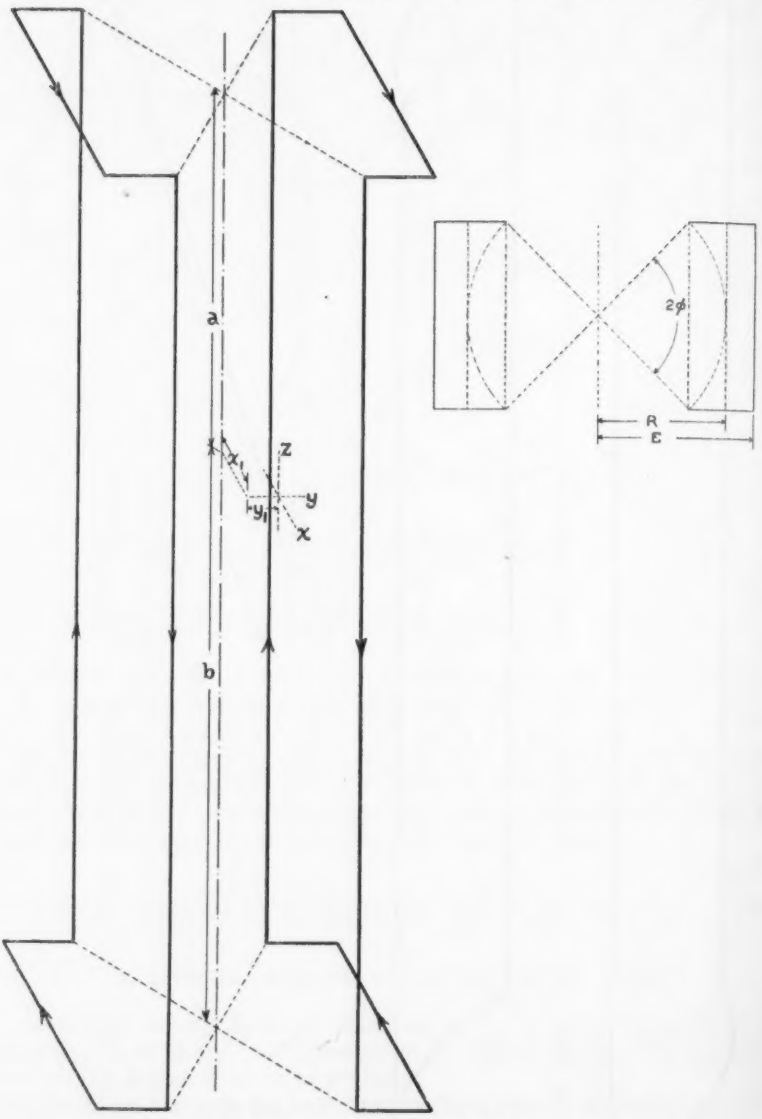

FIGURE 4.—*Bent-head coils.*

The x-component and z-component of the field are again zero.

For points not on the axis of the coils the field can be expressed in terms of infinite series.[3] That expression is not, however, convenient for computing, and an approximation has been developed for evaluating the field in this case. This approximation requires the use of

[3] See appendix.

material in the section immediately below, and will therefore be discussed later.

4. BENT-HEAD COILS

A coil pair of the type shown in figure 4 can be wound as rectangular coils and the ends then bent back to form the rectangular heads shown in the figure. For our purposes it will be necessary to consider only coils shaped so that $E \geqslant R$, since for smaller values of E the field set up by the coils is increasingly less uniform.

The expression for the field set up by the coils is

$$
\begin{aligned}
\frac{RH_x}{I} = &-\frac{K}{A}\left[\frac{c}{\sqrt{(c^2+A)}}+\frac{d}{\sqrt{(d^2+A)}}\right]+\frac{K}{B}\left[\frac{c}{\sqrt{(c^2+B)}}+\frac{d}{\sqrt{(d^2+B)}}\right]\\
&+\frac{L}{C}\left[\frac{c}{\sqrt{(c^2+C)}}+\frac{d}{\sqrt{(d^2+C)}}\right]-\frac{L}{D}\left[\frac{c}{\sqrt{(c^2+D)}}+\frac{d}{\sqrt{(d^2+D)}}\right]\\
&+\frac{c}{c^2+M^2}\left[\frac{F}{\sqrt{(c^2+P)}}-\frac{G}{\sqrt{(c^2+Q)}}+\frac{L}{\sqrt{(c^2+C)}}-\frac{K}{\sqrt{(c^2+A)}}\right]\\
&-\frac{c}{c^2+N^2}\left[\frac{F}{\sqrt{(c^2+R)}}-\frac{G}{\sqrt{(c^2+S)}}+\frac{L}{\sqrt{(c^2+D)}}-\frac{K}{\sqrt{(c^2+B)}}\right]\\
&+\frac{d}{d^2+M^2}\left[\frac{F}{\sqrt{(d^2+P)}}-\frac{G}{\sqrt{(d^2+Q)}}+\frac{L}{\sqrt{(d^2+C)}}-\frac{K}{\sqrt{(d^2+A)}}\right]\\
&-\frac{d}{d^2+N^2}\left[\frac{F}{\sqrt{(d^2+R)}}-\frac{G}{\sqrt{(d^2+S)}}+\frac{L}{\sqrt{(d^2+D)}}-\frac{K}{\sqrt{(d^2+B)}}\right]\\
\frac{RH_y}{I} = &\frac{M}{A}\left[\frac{c}{\sqrt{(c^2+A)}}+\frac{d}{\sqrt{(d^2+A)}}\right]+\frac{N}{B}\left[\frac{c}{\sqrt{(c^2+B)}}+\frac{d}{\sqrt{(d^2+B)}}\right]\\
&+\frac{M}{C}\left[\frac{c}{\sqrt{(c^2+C)}}+\frac{d}{\sqrt{(d^2+C)}}\right]+\frac{N}{D}\left[\frac{c}{\sqrt{(c^2+D)}}+\frac{d}{\sqrt{(d^2+D)}}\right]\\
&+\frac{c}{c^2+F^2}\left[\frac{M}{\sqrt{(c^2+P)}}+\frac{N}{\sqrt{(c^2+R)}}\right]+\frac{c}{c^2+G^2}\left[\frac{M}{\sqrt{(c^2+Q)}}\right.\\
&\left.+\frac{N}{\sqrt{(c^2+S)}}\right]+\frac{d}{d^2+F^2}\left[\frac{M}{\sqrt{(d^2+P)}}+\frac{N}{\sqrt{(d^2+R)}}\right]\\
&+\frac{d}{d^2+G^2}\left[\frac{M}{\sqrt{(d^2+Q)}}+\frac{N}{\sqrt{(d^2+S)}}\right]\\
\frac{RH_z}{I} = &-\frac{M}{c^2+M^2}\left[\frac{F}{\sqrt{(c^2+P)}}-\frac{G}{\sqrt{(c^2+Q)}}+\frac{L}{\sqrt{(c^2+C)}}-\frac{K}{\sqrt{(c^2+A)}}\right]\\
&-\frac{N}{c^2+N^2}\left[\frac{F}{\sqrt{(c^2+R)}}-\frac{G}{\sqrt{(c^2+S)}}+\frac{L}{\sqrt{(c^2+D)}}-\frac{K}{\sqrt{(c^2+B)}}\right]\\
&+\frac{M}{d^2+M^2}\left[\frac{F}{\sqrt{(d^2+P)}}-\frac{G}{\sqrt{(d^2+Q)}}+\frac{L}{\sqrt{(d^2+C)}}-\frac{K}{\sqrt{(d^2+A)}}\right]\\
&+\frac{N}{d^2+N^2}\left[\frac{F}{\sqrt{(d^2+R)}}-\frac{G}{\sqrt{(d^2+S)}}+\frac{L}{\sqrt{(d^2+D)}}-\frac{K}{\sqrt{(d^2+B)}}\right]\\
&-\frac{F}{c^2+F^2}\left[\frac{M}{\sqrt{(c^2+P)}}+\frac{N}{\sqrt{(c^2+R)}}\right]+\frac{G}{c^2+G^2}\left[\frac{M}{\sqrt{(c^2+Q)}}\right.\\
&\left.+\frac{N}{\sqrt{(c^2+S)}}\right]+\frac{F}{d^2+F^2}\left[\frac{M}{\sqrt{(d^2+P)}}+\frac{N}{\sqrt{(d^2+R)}}\right]\\
&-\frac{G}{d^2+G^2}\left[\frac{M}{\sqrt{(d^2+Q)}}+\frac{N}{\sqrt{(d^2+S)}}\right]
\end{aligned}
\tag{6}
$$

Here, in addition to the symbols already defined, we have

$1-g+\epsilon=F;\ 1+g+\epsilon=G;$
$\sin^2\phi+h-2g-s+2\epsilon(1-g+\epsilon/2)=P;$
$\sin^2\phi+h+2g-s+2\epsilon(1+g+\epsilon/2)=Q;$
$\sin^2\phi+h-2g+s+2\epsilon(1-g+\epsilon/2)=R;$
$\sin^2\phi+h+2g+s+2\epsilon(1+g+\epsilon/2)=S;$

where (referring to fig. 4) $\epsilon=\dfrac{E}{R}-1$

At the axis equations 6 reduce to

$$H_x=O$$

$$\frac{RH_y}{I}=$$

$$4\sin\phi\left[\frac{c}{\sqrt{(1+c^2)}}\left(1+\frac{1}{\sqrt{(1+c^2)}\sqrt{(\{1+\epsilon\}^2+c^2+\sin^2\phi)}\left(1+\frac{2\epsilon+\epsilon^2}{1+c^2}\right)}\right)\right.$$
$$\left.+\frac{d}{\sqrt{(1+d^2)}}\left(1+\frac{1}{\sqrt{(1+d^2)}\sqrt{(\{1+\epsilon\}^2+d^2+\sin^2\phi)}\left(1+\frac{2\epsilon+\epsilon^2}{1+d^2}\right)}\right)\right] \quad (7)$$

$$H_z=O$$

5. CIRCULAR-HEAD COILS (APPROXIMATION)

If, for the coils of figure 4, we set $E=R$ ($\epsilon=0$), and if at the same time, we consider the coil shape shown in figure 2 we will have two coil shapes (figs. 2 and 4) between which the circular-head coil pair of figure 3 is intermediate. The long sides of the coils are coincident in the three cases and the end effect for the circular-head coils is intermediate between the end effects in the boundary cases of figures 2 and 4.

The field at the axis of the bent-head coils for the boundary case ($\epsilon=0$) may be written immediately from equation 7.

$$\frac{RH_y}{I}=4\sin\phi\left[\frac{c}{\sqrt{(1+c^2)}}\left(1+\frac{1}{\sqrt{(1+c^2)}\sqrt{(1+c^2+\sin^2\phi)}}\right)+\frac{d}{\sqrt{(1+d^2)}}\right.$$
$$\left.\left(1+\frac{1}{\sqrt{(1+d^2)}\sqrt{(1+d^2+\sin^2\phi)}}\right)\right] \quad (8)$$

Let $H_1(x,y,z)$ denote any particular component of field at the point $P(x,y,z)$ for the straight-head coils, let $H_2(x,y,z)$ denote the same component of field at P for the circular-head coils, and $H_3(x,y,z)$ that for the bent-head coils with $\epsilon=0$. Now $H_2(x,y,z)$ cannot conveniently be computed (except for points (o,o,z) on the axis) but is intermediate between $H_1(x,y,z)$ and $H_3(x,y,z)$, which can be computed from equations 2 and 6, respectively.

The following method of approximating to any component of $H_2(x,y,z)$ suggests itself and has been adopted. If we define a function $K(x,y,z)$ by

$$K(x,y,z)=\frac{H_2(x,y,z)-H_3(x,y,z)}{H_1(x,y,z)-H_3(x,y,z)} \quad (9)$$

then

$$H_2(x,y,z) = H_3(x,y,z) + K(x,y,z)[H_1(x,y,z) - H_3(x,y,z)] \qquad (9a)$$

For points on the axis equation 9a becomes

$$H_2(o,o,z) = H_3(o,o,z) + K(o,o,z)[H_1(o,o,z) - H_3(o,o,z)] \qquad (9b)$$

It will be noted that $H_1(o,o,z)$, $H_2(o,o,z)$, and $H_3(o,o,z,)$ can be computed from equations 3, 5, and 8, respectively. Hence $K(o,o,z)$ can be evaluated at the axis for the y-component of field. The $K(o,o,z)$ thus computed is less than unity and varies rather slowly with z.[4] The y-component of field at points near the axis (x and y small) can be closely approximated by using $K(o,o,z)$ in place of $K(x,y,z)$ in equation 9a thus,

$$H_2(x,y,z) \approx H_3(x,y,z) + K(o,o,z)[H_1(x,y,z) - H_3(x,y,z)] \qquad (10)$$

$H_1(x,y,z)$ being computed from equation 2 and $H_3(x,y,z)$ from equation 6 with $\epsilon = 0$. That this approximation is good for small values of x and y is evident from the following considerations. The difference $H_1 - H_3$ is small compared to H_3. Near the axis $K(x,y,z)$ differs by only a small quantity from $K(o,o,z)$ since it is a continuous function of (x,y,z). Hence only terms of higher order than $H_1 - H_3$ are neglected.

The x-component and z-component of field at the point (x, y, z) may also be approximated from equation 10 if $K\ (x, y, z)$ be assumed to have for them the value $K\ (o, o, z)$ computed at the axis for the y-component. This assumption may be justified as yielding a sufficiently good approximation for practical purposes by the check obtained between computed and experimental values for the case discussed in the following section.

III. FIELD UNIFORMITY

Computations have been carried out for the particular case of a pair of circular-head coils such as that shown in figure 3, for which the length [5] is $9R$ and $\phi = \pi/4$.

As a check on the computations and on the approximation just outlined, a pair of coils was set up, and by means of a search coil, the field over a considerable distance around the axis was mapped.

The set-up used for this purpose is shown schematically in figure 5. Current at a frequency of 1,000 cycles per second was sent through the coils and the emf induced in the search coil was balanced by means of the mutual inductor. In order to obtain silence in the phones at the balance point, it was necessary to insert a small quadrature voltage from the drop across a resistance. The field strength for any position of the search coil was computed from the reading of the mutual inductor. The reproducibility of the results was limited to about 1 percent by the precision with which the coordinates and plane of the search coil could be located.

[4] In the case discussed below, for which computations have been carried out, the value of $K(o,o,z)$ was found to vary from about 0.2 near the coil heads to 0.3 at the center.

[5] This ratio was used in the compensating coils set up for a cathode-ray oscillograph (see footnote 2) and will show in general the field distribution within any coil pair of this type. The ratio of length to radius for any specific case would be expected to depend on the particular problem in compensation involved.

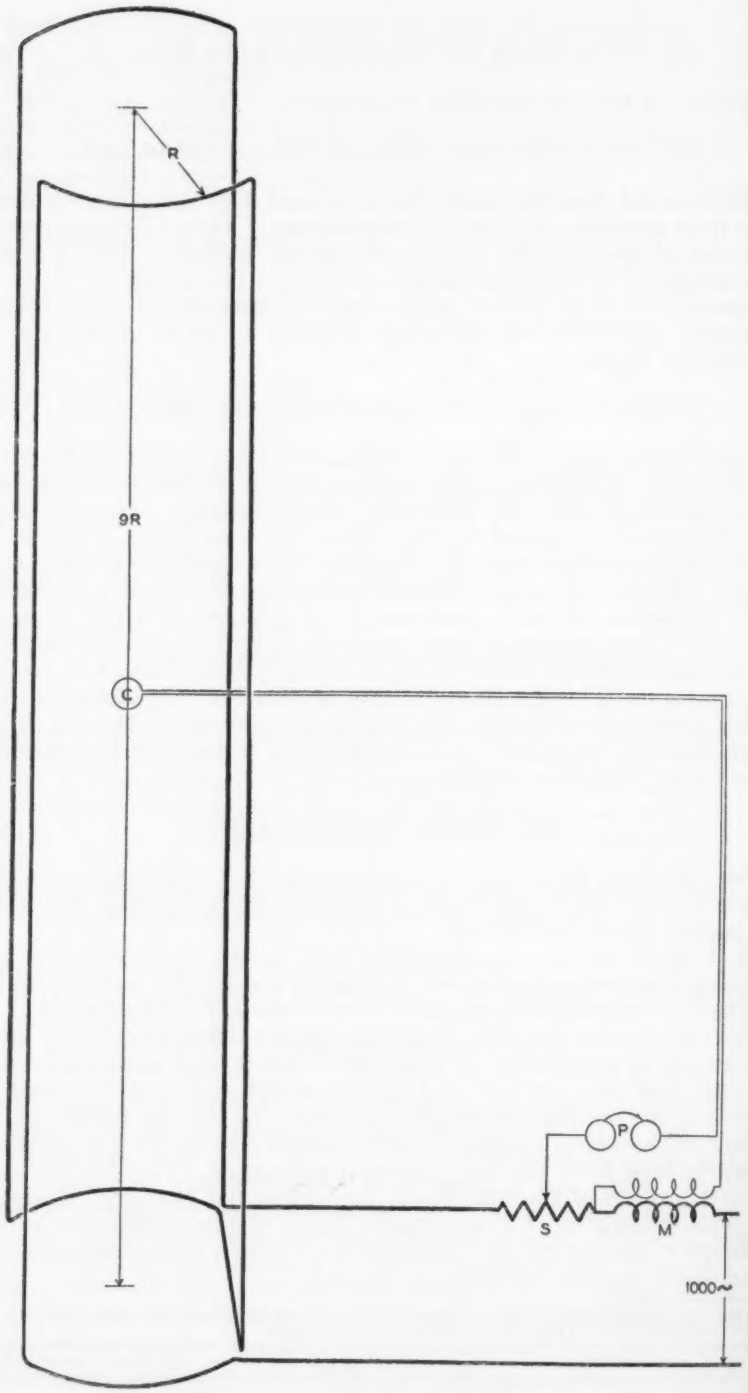

FIGURE 5.—*Diagram of connections for experimental determination of field.*
C, search coil; M, variable mutual inductor; S, variable shunt; P, telephone receiver.

That the approximation outlined in section II–5 is adequate, appears from figures 6, 7, and 8 in which are shown the results of the comparison between computed and experimental field values within the circular-head coils of figure 3.

Figure 6 is a contour map of the y-component of the field for a horizontal plane midway between the coil heads. The contour lines are drawn from computed values, with the value at the center arbitrarily fixed at 100. The solid circles represent experimental values of the field. Each plotted point represents the average of 4 deter-

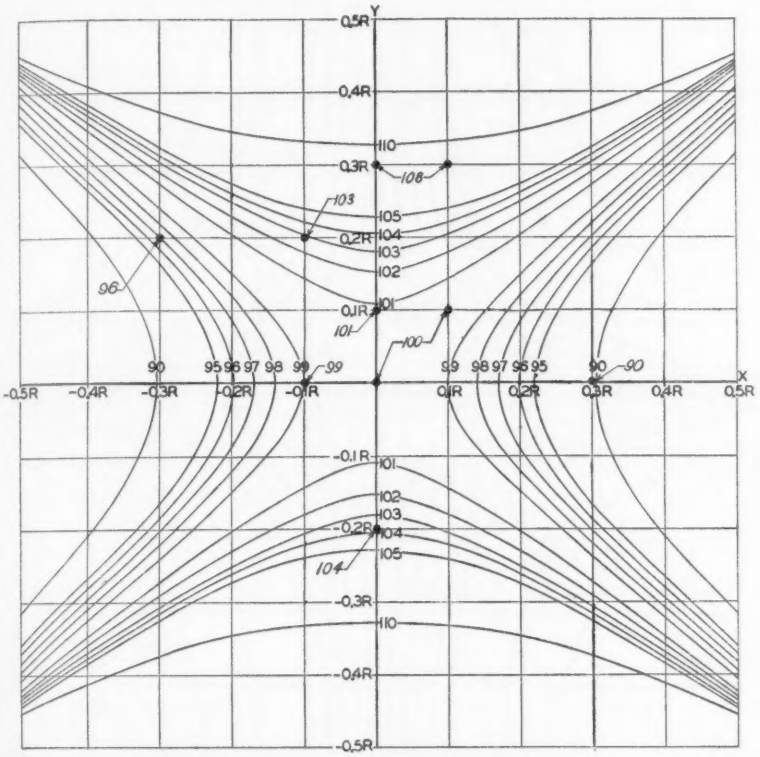

FIGURE 6.—*y-component of field in transverse median plane of circular-head coils.* Numbers attached to contour lines and to points represent computed and experimental field values, respectively.

minations, 1 in each quadrant. The spread of these individual determinations amounts to a percent or less.

The x-component of the field in the same plane is shown in figure 7. Here the field is zero at the center and reverses in direction on passing from one quadrant to the next. The z-component of the field is zero throughout this plane.

Figure 8 shows the three components of the field plotted against vertical distance below the upper coil head for the entire length of the coils. The y-component is plotted along the axis. The x-component and z-component are both zero along the axis and so are plotted for values along vertical lines at the positions indicated by the coordinates at the top of each plot.

The left-hand side of figure 9 shows the uniformity of the resultant field. The solid lines are the traces of figures of revolution within which the resultant field does not depart from the value at the axis and midway between the coil heads by more than the percentage stated on each contour line. For example, within the inner spindle-shaped figure extending over about 0.4 of the coil length, the y-component of the field does not vary by more than 1 percent from the value which it has at the point $(0, 0.5L)$ and the x-component and z-component of the field are each less than 1 percent of the y-compo-

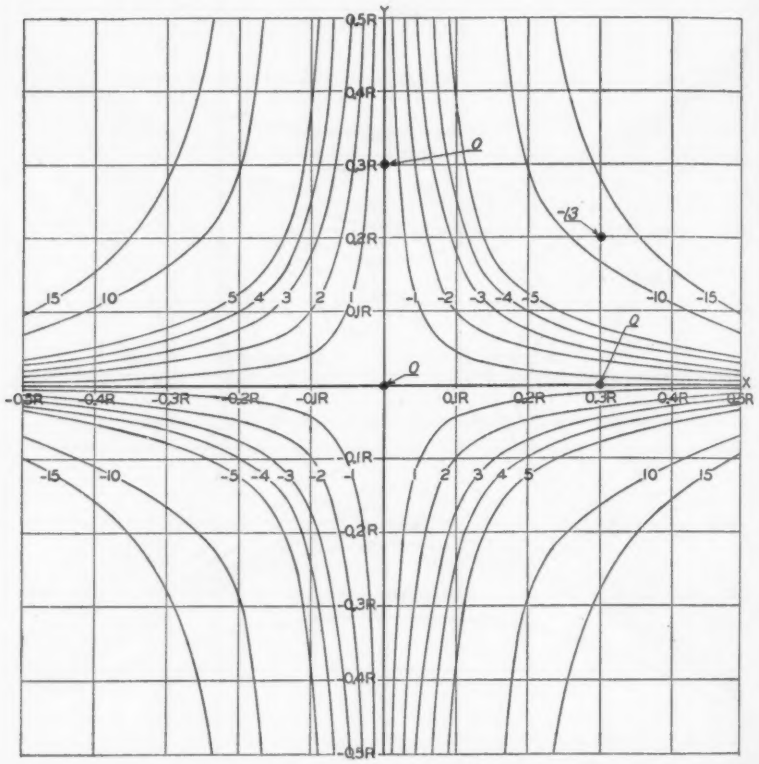

FIGURE 7.—*x-component of field in transverse median plane of circular-head coils.*
Numbers attached to contour lines and to points represented computed and experimental field values, respectively.

nent. If a field variation of 3 percent is permitted over the cylinder within which compensation is desired 0.85 of the coil length may be used.

The constriction in the upper portion of the figures is a result of the saddle-back shape of the y-component of the field along the axis as shown in figure 8. An equal constriction exists for the lower end of the coil, which is not shown in figure 9.

The right-hand side of figure 9 shows tne uniformity of the field for the coil pair with rectangular heads bent back so as to be just tangent to the arc used in the circular-head coils. This is the coil shape shown in figure 4 with $\epsilon=0$ and is the outer boundary case which was used in the approximation of section II–5. It will be seen that

the coil length over which the field variation is less than 2 percent is increased, by the change in shape, from 0.6 of the coil length to 0.8 of the coil length. The constriction in the upper part of the figure has

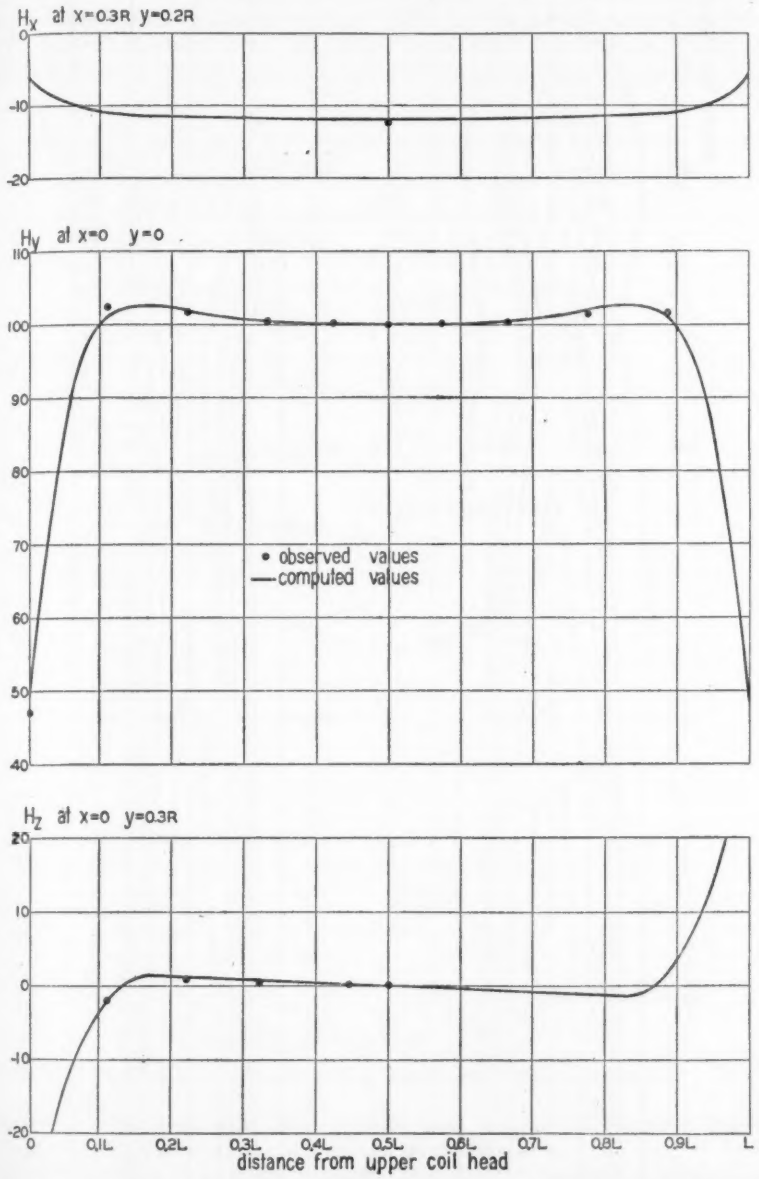

FIGURE 8.—*Variation of field components with distance from coil head for circular-head coils.*

been considerably reduced from the circular-head case but at the cost of shortening the figure somewhat.

Uniformity of the field within the coils can be improved by a further modification of the coil head. If the return lead in the head

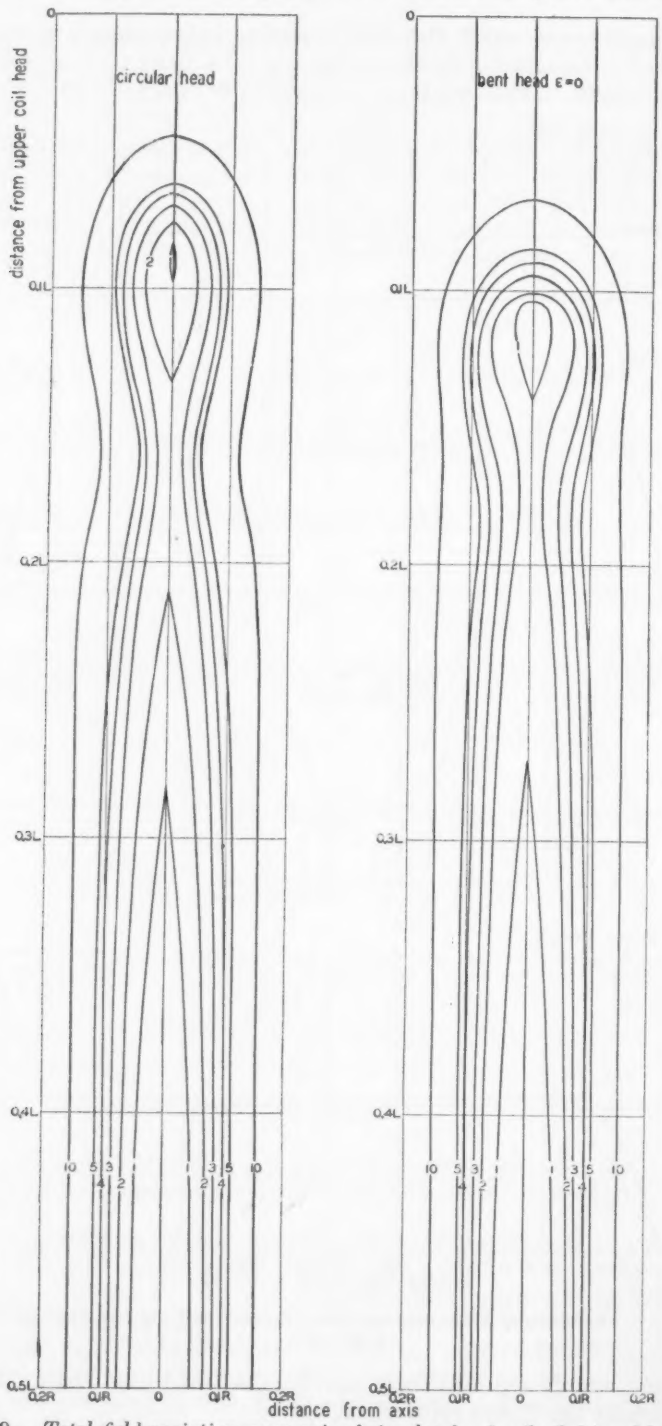

FIGURE 9.—*Total field variation near axis of circular-head coils (left) and bent-head coils (right).*

Numbers attached to contour lines represent field values.

is moved back farther from the axis, i.e., if ϵ is increased, the constriction shown in figure 9 is decreased. However as this constriction decreases it moves in toward the center of the coil to decrease the total length over which the field is effectively uniform. The exact point at which a gain in field uniformity, resulting from an increase of ϵ, ceases must be determined from the conditions imposed by any particular problem in compensation. This is shown in figure 10. In this figure

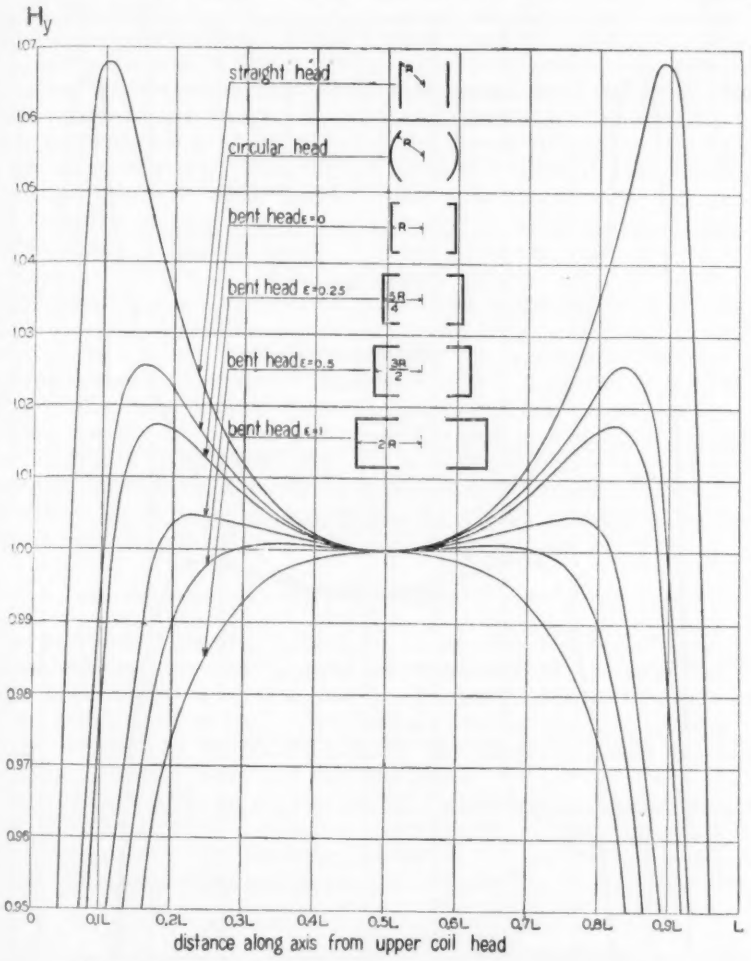

FIGURE 10.—*Variation of y-component of field along axis.*

the y-component of the field at the axis is plotted against vertical distance along the coil for a variety of coil heads.

It will be seen that if uniformity to within 1 percent is desired the coil pair corresponding to $\epsilon=0.25$ has nearly the optimum shape. In this case, compensation of a uniform local magnetic field to within 1 percent could be secured over a circular cylinder whose length is approximately 0.7 of the coil length and whose diameter is approximately 0.05 of the distance between diagonally-opposite corners of the coil pair.

IV. CHOICE OF COIL SHAPE

It is apparent from the results given above that the coil shape described by Beyerle is not the shape best adapted for compensating the local magnetic field over a long cylindrical volume. A coil of the type designated above as bent-head is simpler to construct, since it

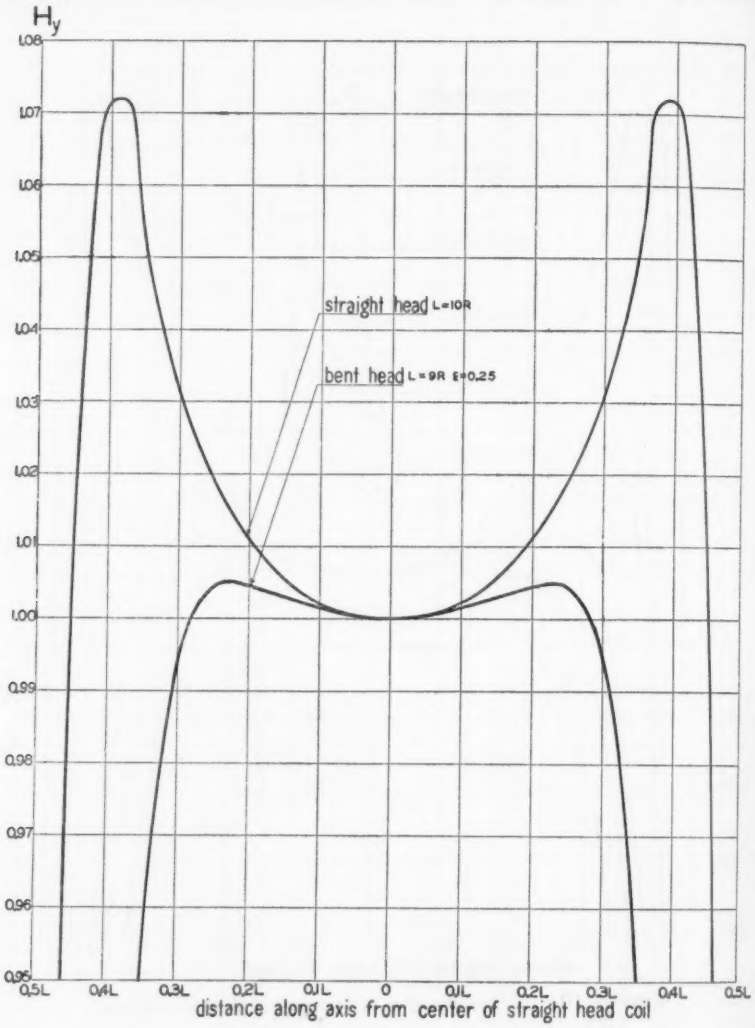

FIGURE 11.—*Variation of y-component of field along axis.*

can be wound on a rectangular form and the ends then be bent back a proper distance. Furthermore, for a coil which occupies the same space, i.e., with $\epsilon=0$, there is a distinct gain in the uniformity of the field which is set up close to the axis as compared with the field resulting from the circular-head coils. If a more uniform field is desired heads can be formed with $\epsilon>0$ by bending back the ends of the rectangular coils at an appropriate point.

There is also a gain in uniformity of field in bending back the coil ends as compared with rectangular coils having the same total length of wire. This is shown in figure 11. Here the field along the axis is shown for two cases: (1), for the straight-head coils shown in figure 2; and (2), for the same coils with the ends bent back as shown in figure 4 with $\epsilon=0.25$. It will be seen that the length over which the field is uniform to within 1 percent is 50 percent greater in the second case than in the first.

By the aid of equation 7 and of figures 9 and 10 it should be possible to design coils which, for a straight electron beam, will effectively neutralize the component of the local magnetic field perpendicular to the direction of the beam. When the diameter of the cylinder over which compensation is desired and the degree of uniformity needed for the compensating field are known, the diameter of the coils can be fixed from figure 9. The length of the coils can then be tentatively fixed from the length of the cylinder which must have a uniform field, and the shape of the coil heads from the degree of uniformity needed, by the aid of figure 10. Since, however, figures 9 and 10 have been constructed for coils whose ratio of length to radius is 9, it may be advisable when the coils are to have a ratio greatly different from that to check one's conclusions by computing by means of equation 7 the field distribution of a pair of bent-head coils having the desired ratio.

It must be remembered that the analysis given above was worked out for a specific problem in compensation and, except for the formulas given, does not claim generality. It is hoped that the data which are presented are sufficient to indicate the general characteristics of the field and to assist in the design of coils for other cases where magnetic compensation is needed over a long, narrow cylinder.

APPENDIX

The solution of the magnetic field in the case of circular-head coils is considerably more complicated for points not on the axis than the simple solution given in equation 5. Here we need to consider only the coil heads themselves. The field due to the straight sides of the coils is included in the cases already discussed and may be added directly to the field found for the coil heads.

We must first write an expression for the field at any point resulting from a current flowing through a circular arc. Using Ampere's law, as already stated, and referring to figure 12, we have, for the arc forming the upper right coil head,

$$\frac{H}{I}=-\mathbf{i}\int_{-\phi_1}^{\phi_1}\frac{aR\sin\phi d\phi}{[u^2+a^2+2R(x_1\sin\phi-y_1\cos\phi)]^{\frac{3}{2}}}$$
$$+\mathbf{j}\int_{-\phi_1}^{\phi_1}\frac{aR\cos\phi d\phi}{[u^2+a^2+2R(x_1\sin\phi-y_1\cos\phi)]^{\frac{3}{2}}}$$
$$+\mathbf{k}\int_{-\phi_1}^{\phi_1}\frac{(y_1\cos\phi-x_1\sin\phi-R)Rd\phi}{[u^2+a^2+2R(x_1\sin\phi-y_1\cos\phi)]^{\frac{3}{2}}}$$

where $u^2=x_1^2+y_1^2+R^2$.

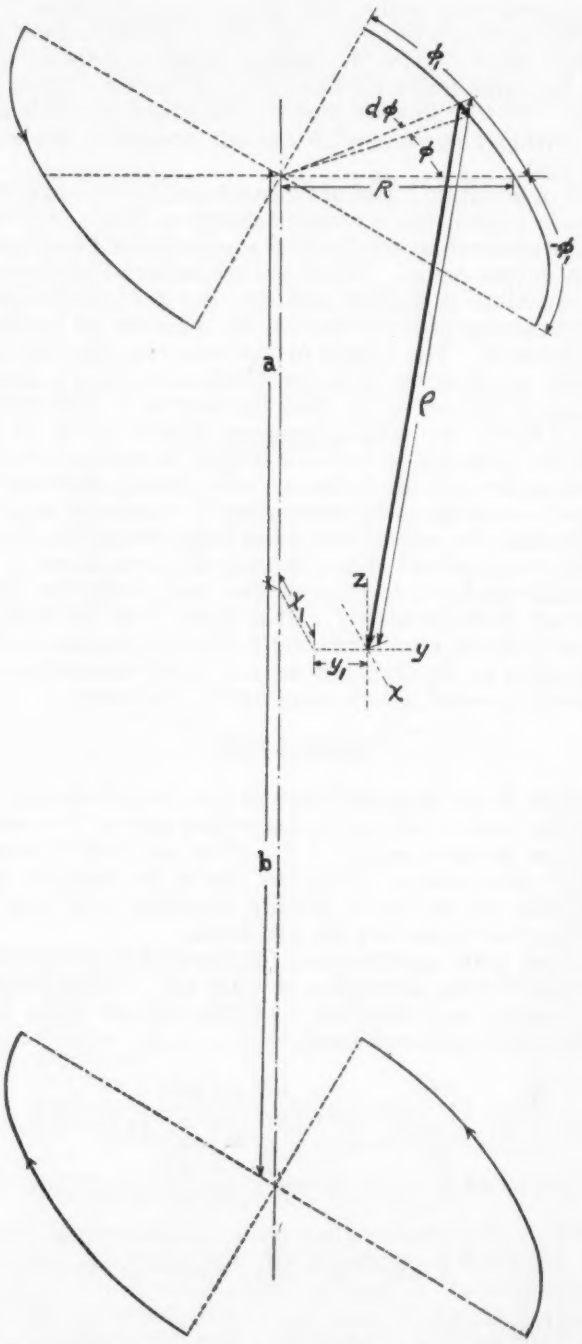

FIGURE 12.—*Curved end sections of circular-head coils.*

On combining the fields resulting from the four arcs forming the coil heads and reverting to the coordinates and nomenclature previously defined we may express the total end effect as

$$\frac{RH_x}{I} = -\int \frac{c \sin \phi d\phi}{[c^2+h+2(f \sin \phi - g \cos \phi)]^{\frac{3}{2}}} - \int \frac{d \sin \phi d\phi}{[d^2+h+2(f \sin \phi - g \cos \phi)]^{\frac{3}{2}}}$$
$$- \int \frac{c \sin \phi d\phi}{[c^2+h-2(f \sin \phi - g \cos \phi)]^{\frac{3}{2}}} - \int \frac{d \sin \phi d\phi}{[d^2+h-2(f \sin \phi - g \cos \phi)]^{\frac{3}{2}}}$$

$$\frac{RH_y}{I} = \int \frac{c \cos \phi d\phi}{[c^2+h+2(f \sin \phi - g \cos \phi)]^{\frac{3}{2}}} + \int \frac{d \cos \phi d\phi}{[d^2+h+2(f \sin \phi - g \cos \phi)]^{\frac{3}{2}}}$$
$$+ \int \frac{c \cos \phi d\phi}{[c^2+h-2(f \sin \phi - g \cos \phi)]^{\frac{3}{2}}} + \int \frac{d \cos \phi d\phi}{[d^2+h-2(f \sin \phi - g \cos \phi)]^{\frac{3}{2}}}$$

$$\frac{RH_z}{I} = \int \frac{(g \cos \phi - f \sin \phi - 1) d\phi}{[c^2+h+2(f \sin \phi - g \cos \phi)]^{\frac{3}{2}}} - \int \frac{(g \cos \phi - f \sin \phi - 1) d\phi}{[d^2+h+2(f \sin \phi - g \cos \phi)]^{\frac{3}{2}}}$$
$$+ \int \frac{(g \cos \phi - f \sin \phi + 1) d\phi}{[c^2+h-2(f \sin \phi - g \cos \phi)]^{\frac{3}{2}}} - \int \frac{(g \cos \phi - f \sin \phi + 1) d\phi}{[d^2+h-2(f \sin \phi - g \cos \phi)]^{\frac{3}{2}}}$$

where all the integrals are taken between the limits $-\phi_1$ and ϕ_1.

Since the approximation given above has been found satisfactory it will suffice here to work out only the y-component of the field. The x-component and z-component may be obtained by a procedure similar to that indicated below.

We will solve the integrals containing c and the solution for the integrals in d may be obtained by substitution. We have, then

$$\int \frac{c \cos \varphi d\varphi}{[c^2+h+2(f \sin \varphi - g \cos \varphi)]^{\frac{3}{2}}} + \int \frac{c \cos \varphi d\varphi}{[c^2+h-2(f \sin \varphi - g \cos \varphi)]^{\frac{3}{2}}}.$$

If we let

$$\frac{f}{\sqrt{(h-1)}} = \cos \alpha; \quad \frac{g}{\sqrt{(h-1)}} = \sin \alpha; \quad \beta = \varphi - \alpha;$$

we have

$$\frac{cf}{\sqrt{(h-1)}}\left[\int \frac{\cos \beta d\beta}{[c^2+h+2\sqrt{(h-1)} \sin \beta]^{\frac{3}{2}}} + \int \frac{\cos \beta d\beta}{[c^2+h-2\sqrt{(h-1)} \sin \beta]^{\frac{3}{2}}}\right]$$
$$- \frac{cg}{\sqrt{(h-1)}}\left[\int \frac{\sin \beta d\beta}{[c^2+h+2\sqrt{(h-1)} \sin \beta]^{\frac{3}{2}}} + \int \frac{\sin \beta d\beta}{[c^2+h-2\sqrt{(h-1)} \sin \beta]^{\frac{3}{2}}}\right].$$

The first expression integrates immediately to

$$\frac{cf}{h-1}\left[\frac{1}{\sqrt{(c^2+h-2\{f \sin \varphi - g \cos \varphi\})}} - \frac{1}{\sqrt{(c^2+h+2\{f \sin \varphi - g \cos \varphi\})}}\right]_{-\varphi_1}^{\varphi_1}$$

which yields on application of the limits [6]

$$\frac{cf}{h-1}\left[\frac{1}{\sqrt{(c^2+A)}}-\frac{1}{\sqrt{(c^2+B)}}+\frac{1}{\sqrt{(c^2+C)}}-\frac{1}{\sqrt{(c^2+D)}}\right].$$

We may integrate the second expression as an infinite series by expanding into a power series an expression of the type

$$\frac{\sin\beta}{p+q\sin\beta]^{\frac{1}{2}}}=\sin\beta-\frac{3}{2}\frac{q}{p}\sin^2\beta+\frac{3\cdot5}{2\cdot4}\left(\frac{q}{p}\right)^2\sin^3\beta-\cdots\cdots\cdots$$

The resulting expressions may now be combined with that for the field resulting from the straight sections of the coils obtained from equation 2. For the special case considered experimentally ($\phi=\pi/4$) the complete expression for the y-component of the field is the following

$$\begin{aligned}
\frac{RH_y}{I}&-\frac{M}{A}\left[\frac{c}{\sqrt{(c^2+A)}}+\frac{d}{\sqrt{(d^2+A)}}\right]+\frac{N}{B}\left[\frac{c}{\sqrt{(c^2+B)}}+\frac{d}{\sqrt{(d^2+B)}}\right]\\
&+\frac{M}{C}\left[\frac{c}{\sqrt{(c^2+C)}}+\frac{d}{\sqrt{(d^2+C)}}\right]+\frac{N}{D}\left[\frac{c}{\sqrt{(c^2+D)}}+\frac{d}{\sqrt{(d^2+D)}}\right]\\
&+\frac{cf}{h-1}\left[\frac{1}{\sqrt{(c^2+A)}}-\frac{1}{\sqrt{(c^2+B)}}+\frac{1}{\sqrt{(c^2+C)}}-\frac{1}{\sqrt{(c^2+D)}}\right]\\
&+\frac{df}{h-1}\left[\frac{1}{\sqrt{(d^2+A)}}-\frac{1}{\sqrt{(d^2+B)}}+\frac{1}{\sqrt{(d^2+C)}}-\frac{1}{\sqrt{(d^2+D)}}\right]\\
&+\frac{2\sqrt{(2)}cg^2}{(h-1)(c^2+h)^{\frac{1}{2}}}\left[1+\frac{5}{2}\frac{(h-1)}{(c^2+h)^2}\left\{\frac{(g^2-f^2)}{2(h-1)}+2\right\}\right.\\
&+\frac{63}{8}\frac{(h-1)^2}{(c^2+h)^4}\left\{\frac{(g^2-f^2)}{4(h-1)^2}(g^2+3f^2)+\frac{2(g^2-f^2)}{3(h-1)}+\frac{8}{3}\right\}\\
&+\frac{429}{16}\frac{(h-1)^3}{(c^2+h)^6}\left\{\frac{(g^2-f^2)}{8(h-1)^3}(g^4+10f^2g^2+5f^4)\right.\\
&\left.\left.+\frac{3(g^2-f^2)}{10(h-1)^2}(g^2+3f^2)+\frac{4(g^2-f^2)}{5(h-1)}+\frac{16}{5}\right\}+\cdots\cdots\cdots\cdots\right]\\
&+\frac{2\sqrt{(2)}dg^2}{(h-1)(d^2+h)^{\frac{1}{2}}}\left[1+\frac{5}{2}\frac{(h-1)}{(d^2+h)^2}\left\{\frac{(g^2-f^2)}{2(h-1)}+2\right\}\right.\\
&\left.+\frac{63}{8}\frac{(h-1)^2}{(d^2+h)^4}\left\{\frac{(g^2-f^2)}{4(h-1)^2}(g^2+3f^2)+\frac{2(g^2-f^2)}{3(h-1)}+\frac{8}{3}\right\}+\cdots\cdots\right]
\end{aligned}$$

A number of field values were computed with this formula and found to agree to within about 0.1 percent with the corresponding values computed by means of the approximation described earlier in the paper. These values ranged as far as $0.4R$ from the axis. It can therefore be stated that the approximation given in section II-5 is sufficiently accurate for computing the field at the small distances from the axis that are of particular importance.

WASHINGTON, June 25, 1934.

[6] See definitions after equation 2 above.

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FORMS OF RUBBER AS INDICATED BY TEMPERATURE-VOLUME RELATIONSHIP

By Norman Bekkedahl

ABSTRACT

Temperature-volume measurements were made from −85 to +85 C on rubber hydrocarbon and 3 soft rubber-sulphur compounds, using dilatometers of a low thermal expansion glass with alcohol, acetone, water, and mercury as confining liquids. Measurements of linear expansion were made on one specimen of rubber hydrocarbon from −190 to 0 C.

These measurements indicate that unvulcanized rubber may exist in at least 4 forms. The familiar form, designated as amorphous I, undergoes slow transition at 6 to 16 C to a form called crystalline I which is the stable modification between −72 and +6 C. At 0 C the transition takes place more rapidly, requiring about 10 days, and is accompanied by a change of volume of 2.65 percent. At about −72 C both the crystalline I and the metastable amorphous I forms undergo transitions, with large decreases in coefficients of expansion, to crystalline II and amorphous II forms, respectively. Vulcanized rubber, in the unstretched state, exhibited only the amorphous I and the amorphous II forms, the compounds containing 2, 4, and 6 percent of combined sulphur undergoing transition at −72, −62, and −53 C, respectively.

The volume coefficient of expansion of rubber in the amorphous I form, from −72 to +85 C, is given by the relation,

$$\frac{dv}{dt}=0.00067+0.0000007\ (t-25)$$

where t is the temperature in degrees C. The volume coefficient for the crystalline I form between −72 and +6 C is approximately 0.00053. Between −72 and −85 C both the amorphous II and the crystalline II forms have approximately the same volume coefficient, 0.00020. The average linear coefficients between −190 and −72 C are 0.000060 for the amorphous II form and 0.000054 for the crystalline II form.

The results of the present investigation afford a basis for correlating and interpreting data obtained by the author and other investigators on the heat capacity, electrical properties, and behavior of rubber on stretching.

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I. INTRODUCTION

This paper describes measurements of the change of volume of rubber with change of temperature, which have been used as a means for determining the forms in which rubber may exist and ascertaining the conditions under which transition from one form to another may occur.

This work is part of a study of the basic thermodynamic properties of rubber which is being conducted at the cryogenic laboratory of the National Bureau of Standards. In this study, an attempt was first made to measure the heat capacity of rubber over a wide range of temperature, but under some circumstances anomalies due to change in phase were encountered which took place so slowly that it was impracticable to follow them through by calorimetric methods. These anomalies have been studied by the measurement of the changes in volume or coefficient of expansion associated with them, it being possible to follow changes in volume over as long a period of time as desired. At temperatures at which rubber is relatively stiff and rigid, measurements of length have been used as an adjunct to the volume measurements.

Measurements of the temperature-volume relations of rubber have been made by several previous investigators who have recognized the existence of rubber in different forms. The contribution of the present investigation lies in the fact that it reports a somewhat more comprehensive and systematic study than has been made previously. The findings are largely in accord with those of the other workers, as will be brought out in a subsequent section of the paper.

The results of the measurements indicate that between -190 and $+85$ C unvulcanized rubber may exist in at least 4 forms. Similar measurements on vulcanized rubber demonstrate the existence of 2 analogous forms, while the behavior on stretching points to the possibility that the other 2 analogous forms may exist in stretched rubber. The temperatures of transition have been determined approximately, and observations have been made on the rates of transition under various circumstances. Thus a foundation has been laid on the basis of which the calorimetric investigations referred to above can be conducted with facility.

The anomalies which have been observed in the temperature-volume measurements of the unstretched rubber find a close counterpart in preliminary measurements of heat capacity by the author, and also in data published by other investigators. Indications of anomalies corresponding to those found in the temperature-volume

studies described in this paper were also found in studies of the electrical and of the mechanical properties of rubber.

II. TYPES OF RUBBER INVESTIGATED

The samples on which measurements were made included crude rubber in the form of smoked sheet, rubber hydrocarbon, and compounds of the latter with sulphur. Rubber hydrocarbon was prepared by the digestion of latex with steam at about 190° C and the subsequent extraction of the resins and the products of hydrolysis with alcohol and water.[1] Where the term rubber hydrocarbon is used without qualification in this paper, this product is understood. The vulcanized samples contained 2, 4, and 6 percent of sulphur, and were prepared from rubber hydrocarbon and sulphur. They were vucanized so as to bring all but a few hundredths of a percent of the sulphur into combination with the rubber.

III. APPARATUS AND EXPERIMENTAL PROCEDURE

The measurements of the change in volume of rubber were made by enclosing samples with suitable confining liquids in dilatometers and observing the changes in height of the liquid in calibrated capillary tubes when the dilatometers and contents were subjected to different temperatures. The dilatometers were made of a laboratory glass having a low coefficient of expansion. The measurements of the change of length were made with the fused quartz tube apparatus described by Hidnert and Sweeney.[2]

1. DESCRIPTION OF DILATOMETERS

The dilatometers were patterned after liquid-in-glass thermometers and consisted of bulbs sealed to capillary tubes as shown in figure 1. In making them, the capillaries were first sealed to tubes about 2 cm in diameter, leaving the end opposite the capillary open. Weighed samples of rubber were then placed inside the tubes and the ends quickly sealed, taking care not to scorch the rubber. The dilatometers containing the samples were weighed, filled to a mark on the capillary with a confining liquid at a given temperature, and again weighed. The volumes of the dilatometers were found from the weights and densities of the samples and confining liquids at a given temperature. Volumes of the dilatometers at other temperatures were computed using the volume of coefficient of expansion for the glass used.[3]

FIGURE 1.—*Dilatometer used for determination of temperature-volume relations of rubber and confining liquids.*

Three sizes of capillaries were used, ranging from about 40 to 90 cm in length and having diameters approximately 0.6, 1.8, and 2.5 mm, respectively. They were

[1] BS. J. Research **8**, 751(1932); RP449.
[2] BS. J. Research **1**, 771(1928); RP29.
[3] Buffington and Latimer, J. Am. Chem. Soc. **48**, 2305(1926).

calibrated in the usual way by measuring the length of a mercury thread of known weight. In the circumstances under which they were used they covered temperature ranges of about 8, 40, and 120 degrees centigrade, respectively. The capillaries of the smaller diameters were used for the measurement of the coefficient of expansion over small intervals of temperature, while the larger were used to make series of observations continuously over a wide range. The smaller capillaries, of course, gave the more precise values.

Density measurements which were required in the course of the investigation were made with a pycnometer of the type described by Ashton, Houston, and Saylor [4] which was found suitable for use not only at or above room temperature, but also at low temperatures.

2. CONFINING LIQUIDS

Water, alcohol, acetone, and mercury were employed as confining liquids in the temperature ranges for which they were respectively suitable. The alcohol was used in three different concentrations. Most of the measurements were made with a product which was taken from the laboratory supply and contained 89 percent of ethanol and 11 percent of water by weight. But to eliminate the possibility that the water content of this product may have influenced the results at low temperatures, measurements were also made with 92.5 percent alcohol and with absolute alcohol as confining liquids. The acetone was of the chemically pure grade and was not further dehydrated or specially purified before use. The density and the volume coefficient of expansion were determined for the particular samples of alcohol and acetone that were employed. The density and the coefficient of expansion of mercury and of water were taken from the International Critical Tables.[5]

3. MEASUREMENT AND CONTROL OF TEMPERATURE

The temperature range covered in this investigation was from about -85 to $+85$ C with the dilatometers, and from -190 to 0 C in the case of length measurements. Measurements of temperature were made by means of calibrated copper-constantan thermocouples, the electromotive force of which was read on a Wenner potentiometer [6] having a precision of better than one microvolt. This is equivalent to a precision of at least 0.04 C. The measuring junction of the thermocouple was mounted in the bath with the dilatometers, and in the rubber sample itself for the length measurements.

The dilatometers were maintained at the desired temperatures by means of liquid baths in dewar flasks. Above the temperature of 0 C, water was used; below this acetone or a eutectic mixture of carbon tetrachloride and chloroform was employed and was cooled with carbon dioxide snow. Temperatures somewhat below those given by the carbon dioxide snow alone were obtained by the additions of small quantities of liquid air.

[4] BS J.Research **11**,233(1933):RP587. This pycnometer is a modification of the one used by Richards, Hall, and Mair, J.Am.Chem.Soc.**50**,3308(1928).
[5] International Critical Tables, First Edition, McGraw-Hill Book Co., New York, **II**,457, and **III**,24.
[6] Rev. Sci. Instruments **3**,109(1932). Also Phys. Rev. **31**,94(1910).

Slow rates of heating were usually obtained at temperatures below those of the room by allowing the baths to warm spontaneously. With efficient dewar flasks a period of 2 or 3 days was required to reach approximately room temperature from −85 C; by using unsilvered dewar flasks more rapid warming was obtained.

The samples for the length measurements were maintained at about −190 C by means of a bath of liquid air. No observations were recorded between −190 and −95 C. Above the latter temperature an acetone bath was used.

4. COMPUTATION OF COEFFICIENT OF EXPANSION

The method of computing the coefficient of expansion of rubber from the readings of the dilatometer is shown by the following example. A dilatometer containing rubber and alcohol gave a linear change of 8.10 cm per degree centigrade in the height of liquid in the capillary for the range from −4 to +4 C. The volume of the dilatometer including one-half of the capillary was 29.462 ml at a temperature of 0 C, found as indicated above. Calibration of the capillary showed 1 cm of the length to be equivalent to 0.003177 ml. The change in volume, therefore, was 0.02573 ml per degree centigrade at a temperature of 0 C for the rubber and alcohol together, or 0.000874 vol/vol/° C.

The change in volume of the alcohol was 0.00108 vol/vol/° C at a temperature of 0 C as determined by measurements in a similar dilatometer.

In the dilatometer containing rubber, the sample weighed 13.032 g and occupied a volume of 14.150 ml at a temperature of 0 C taking the density to be 0.921 [7] at that temperature. By difference, then, the volume of the alcohol at 0 C was 15.312, or the volume fraction of the alcohol 0.520.

The following equation results:

$$(0.520\times 0.00108)+(1-0.520)\,x=0.000874$$

which, when solved, gives

$$x=0.00065.$$

This, then, is taken as the coefficient of expansion of rubber at a temperature of 0 C.

IV. RESULTS WITH UNVULCANIZED RUBBER

The results which were obtained in the studies on unvulcanized rubber indicate that it may exist in different forms. For simplicity and clarity in presentation, a general statement regarding these forms will be made first and this will be followed by a description of the observations and experiments.

1. FORMS OF UNVULCANIZED RUBBER

The temperature-volume measurements on unvulcanized rubber exhibited two types of anomalies. One of these was the well-known freezing of rubber. This was accompanied by a change of volume of about 2.7 percent and was found to occur in the temperature range 6 to 16 C. The transition was half complete at about 11 C and is

[7] See footnote 1, p. 413.

considered for discussion as the 11 C transition. As will be discussed in a subsequent section, the results of other workers show that frozen rubber is crystalline, and it will be so considered throughout this paper,[8] while the ordinary form of rubber will be regarded as amorphous. The crystallization of rubber on cooling is a relatively slow process so it was found possible to deal with the amorphous phase of rubber as well as the crystalline phase at temperatures below 11 C.

The second type of anomaly was observed at about −72 C. When either the amorphous or the crystalline rubber was subjected to temperatures below this, a marked change in the coefficient of expansion was observed, the coefficient below this temperature being only about one-third as great as that above it.

The relation between the relative volumes of these different forms of rubber is shown graphically in figure 2. In this figure the relative

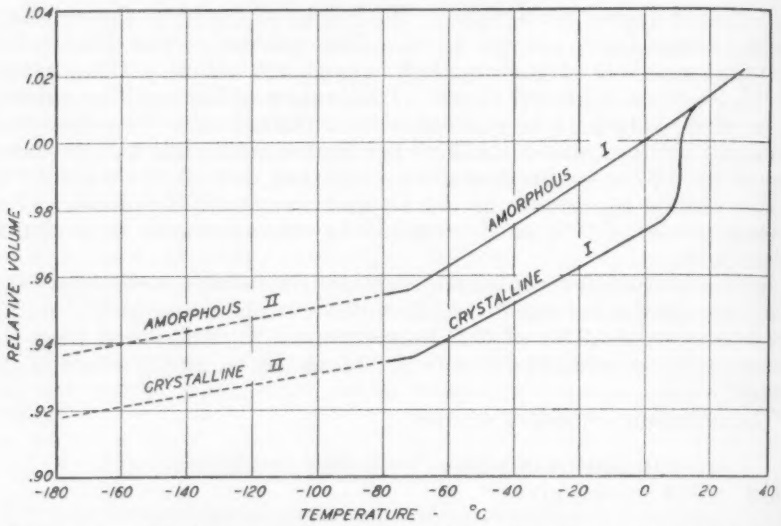

FIGURE 2.—*Relation between volume of rubber hydrocarbon and temperature.*

Below the transition at 11 C the amorphous form is metastable and the crystalline form is stable. The dotted portions of the curves were computed from length measurements.

volume of rubber is plotted as a function of the temperature, taking the volume of rubber as unity in the familiar amorphous form at a temperature of 0 C. As a matter of convenience the various forms of rubber are here designated: The ordinary amorphous form above −72 C is called amorphous rubber I; below −72 C, amorphous rubber II. The crystalline forms are likewise called crystalline rubber I and crystalline rubber II as shown in the figure.

The curves indicate that rubber exists in the amorphous I form at room temperature but that below the transition at 11 C it may either remain in the amorphous I form or undergo transition to the crystalline I form depending on the time and temperature. The crystalline form has the smaller specific volume and is the stable form below about 11 C. The amorphous form is metastable below this tempera-

[8] The product here called the crystalline form of rubber should not be confused with rubber crystals referred to in a recent publication by W. H. Smith, Charles Proffer Saylor, and Henry J. Wing, BS J Research **10**,479(1933); RP544. The former is an agglomerate of crystals with a melting range of about 10 degrees centigrade, while the latter is made up of distinct, individual crystals having relatively sharp melting points.

ture. At about −72 C the crystalline I form undergoes transition to the crystalline II form which is apparently the stable form at low temperatures. At approximately the same transition temperature the amorphous I form changes to the amorphous II form which, although it is evidently metastable, has not been observed to undergo transition to the crystalline II form.

2. MEASUREMENTS OF CHANGES OF VOLUME OF RUBBER

The solid line curves in figure 2 represent measurements which were made on rubber hydrocarbon using the 89 percent alcohol as the confining liquid. The exploration of the temperature range from −80 to +40 C was made with use of a dilatometer having a capillary tube of such capacity that the entire range was covered without the addition or removal of confining liquid. The dotted portions of the curves were computed from length measurements to be described later in the paper. Observations in other ranges were made with dilatometers having small capillaries so that more precise measurements could be made on the coefficients of expansion and on the change in volume. Individual points are not shown for the curves in figure 2 because the amounts by which they deviate from the curves are not appreciable for the scale used. The precision of the measurements is illustrated by figure 3, curve D, in which the portions of the curves showing the transitions from the I forms to the II forms are drawn on a larger scale.

Measurements with acetone, with 92.5 percent alcohol, and with absolute alcohol as confining liquids are also shown in figure 3. The curves with the three concentrations of alcohol all point to a transition at about −72 C, but the curve obtained with acetone gives no indication of a transition. Evidence from changes in length and in other properties with temperature indicates that the results with alcohol, rather than with acetone, represent the true state of affairs. It is possible that the discrepancy is due to the swelling action of acetone on rubber, but further experimental work is required before a definite explanation can be offered.

Measurements on crude rubber gave results closely similar to the above results on rubber hydrocarbon. The freezing occurred in the same temperature range, 6 to 16 C. The I–II transitions of both the amorphous and crystalline rubber occurred at about −72 C. The numerical values of the volume change on crystallization and the coefficient of expansion differed slightly from those for the rubber hydrocarbon as will be indicated in section 5.

3. RATE OF CRYSTALLIZATION OF RUBBER

Observations were made on the rate of crystallization of rubber as indicated by volume measurements at several temperatures, particularly at 0 C. When rubber was cooled from +40 to −72 at a fairly uniform rate in 4 or 5 hours, the volume decreased in a nearly linear manner with the temperature as is shown in the upper curve in figure 2. When it was allowed to warm at the same rate or more rapidly, the volume increased in the same manner. When the rubber was cooled to −72 C as before and allowed to warm at a slower rate, such that 2 or 3 days or more were required to reach room temperature, the volume-temperature relation described this same curve up

to about −25 C. But at some temperature near −25 C, which differed from one experiment to another, the rubber began to decrease in volume with increasing temperature, and continued its decrease until the volume corresponded to that indicated by the lower curve in the figure.

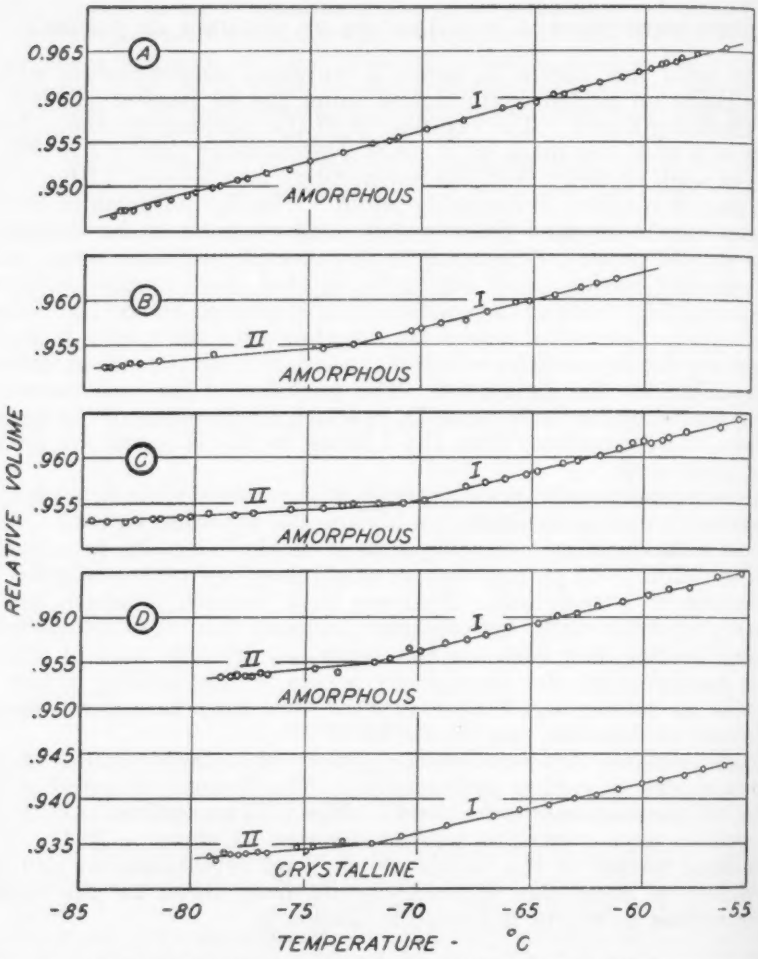

FIGURE 3.—*Relation between volume of rubber hydrocarbon and temperature with different confining liquids in the dilatometers.*

A, acetone; B, absolute alcohol; C, 92.5 percent alcohol; D, 89 percent alcohol. D is a large-scale drawing of a portion of figure 2.

When crystallization was taking place with rising temperature there was a negative coefficient of expansion, and when effected in a calorimeter there was a marked evolution of heat. When the volume decreased to that indicated by the lower curve, the temperature-volume relation was described by that curve. On further heating, the rubber underwent the 11 C transition and returned to its original volume.

Crystallization of rubber seemed to take place most readily at temperatures between −35 and −15 C and was usually complete in a few hours. At the lower part of this range the transition became slower, and at still lower temperatures it did not take place. Samples which were kept below −50 C for 3 weeks gave no indication of transition. One sample which had been cooled to the triple point of hydrogen, −259 C, in a calorimeter, on warming underwent transition at about −35 C indicating that crystallization had not taken place at the lower temperature.

The rate of transition at a temperature of 0 C was measured using dilatometers with alcohol, acetone, mercury, and water, respectively, as confining liquids. The measurements made on rubber hydrocarbon with alcohol as a confining liquid are shown in figure 4 in which the relative volume of rubber is plotted as a function of the time. The curve is S-shaped, which is characteristic of transitions of this type. The change in volume is apparently complete in about

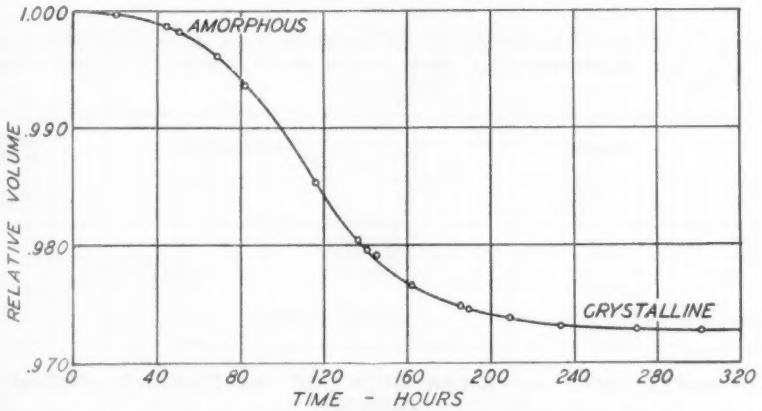

FIGURE 4.—*Decrease in volume with time as rubber hydrocarbon changes from amorphous I to crystalline I form at a temperature of 0 C.*

10 days. This is in quite close agreement with the results of other investigators as will be discussed in section VII. Similar curves were obtained for rubber hydrocarbon with other confining liquids, and also with crude rubber using alcohol as a confining liquid. But when ammonia-preserved rubber latex was kept at a temperature of 0 C for a month no change in volume was observed.

The reverse transition—that is, the one from the crystalline I form to the amorphous I form of rubber—seemed to take place without appreciable delay. Measurements on the rate of transition were made with different rates of warming without significant variation in results. Samples of crude rubber which had been in the crystalline state for several weeks were quickly withdrawn from the ice bath and were placed in water at about 25 C. The stiffness and opacity disappeared within the time required for the samples to reach temperature equilibrium. When crystalline samples were warmed to about 10 C in the dilatometers and cooled again, the temperature-volume relation described exactly the lower curve without lag.

4. CHANGE OF VOLUME OF RUBBER ON CRYSTALLIZATION

The magnitude of the volume change which accompanies the transition of rubber from the amorphous to the crystalline form is indicated by the results previously set forth in figures 2 and 4. The measurements of the change in volume which were made with the different confining liquids at a temperature of 0 C gave somewhat different results for the change in volume depending upon the liquid used. The results are given in table 1. For purified rubber the change was from 2.43 percent with mercury to 2.81 percent with acetone, the average being 2.65 percent. The variation was considerably greater than the probable experimental error and may have been due to the action of the confining liquids on the rubber.

The volume change with crude rubber was 2.20 percent, alcohol being used as the confining liquid. Assuming that crude rubber is 93 percent hydrocarbon, this is equivalent to a volume change of 2.37 percent for the hydrocarbon content.

TABLE 1.—*Decrease in volume in the transition from amorphous to crystalline rubber at a temperature of 0 C when observed in the presence of different confining liquids*

Material	Confining liquid	Decrease in volume
		Percent
Rubber hydrocarbon	Alcohol, 89 percent	2.65
Do	Acetone	2.81
Do	Mercury	2.43
Do	Water	2.70
Average		2.65
Smoked sheet rubber	Alcohol, 89 percent	2.20

5. COEFFICIENT OF EXPANSION OF DIFFERENT FORMS OF RUBBER

Determinations of the volume coefficient of expansion of rubber hydrocarbon in different forms were made in dilatometers provided with small capillary tubes. These tubes were about 75 cm in length and were of such bore that consecutive measurements could be made over a temperature range of about 8 degrees centigrade. To make measurements at other temperatures it was necessary to add or remove confining liquid. The measurements of temperatures below that of the room were made while the dilatometers and their contents were warming slowly, and measurements at higher temperatures while the dilatometers were cooling slowly. The rates of heating and cooling were of the order of 2 degrees centigrade per hour. The bath was stirred constantly so that for practical purposes the contents of the dilatometers may be regarded as being at bath temperatures at all times.

The results are shown in figure 5, in which the volume coefficient of expansion is plotted as a function of the temperature. The coefficients of both the amorphous I and the crystalline I forms bear a nearly linear relation to the temperature, decreasing slightly with decreasing temperature. The coefficient for the crystalline form was not so accurately determined but was found to be about 15 percent lower than that of the amorphous form.

The volume coefficients of expansion for the amorphous I form of rubber between the limits of +85 and −72 C can be calculated from the equation,

$$\frac{dv}{dt} = 0.00067 + 0.0000007(t-25)$$

or its volume may be found from the equation,

$$V_t = V_{25}[1 + 0.00067(t-25) + 0.0000004(t-25)^2]$$

in which $\frac{dv}{dt}$ is the rate of change of volume with temperature, t is the temperature in degrees centigrade, V_t is the volume at the temperature, t, and V_{25} is the volume at 25 C.

At about a temperature of −72 C the coefficients of expansion of each form undergo a marked change, below which both forms have

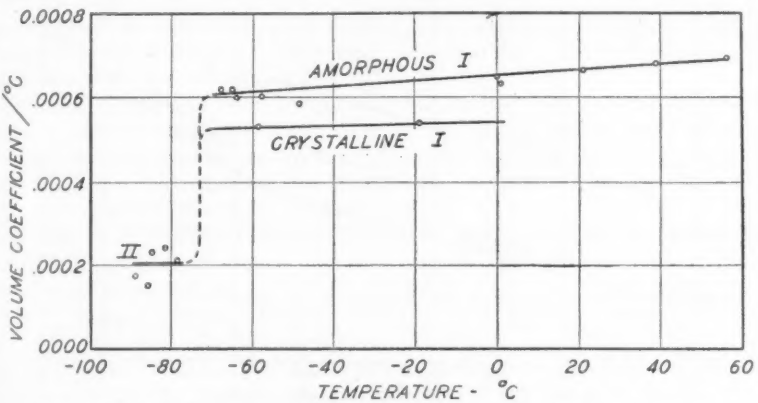

FIGURE 5.—*Relation between coefficients of expansion of different forms of rubber hydrocarbon and temperature.*

values of approximately 0.00020. This latter value was not determined with as great accuracy from volume measurements since they were carried to only about −85 C. The measurements which have thus far been made do not suffice to indicate whether the amorphous I-amorphous II and the crystalline I-crystalline II transitions take place at the same or at slightly different temperatures. No lag was noticed in the transitions between the lower temperature forms and the amorphous I or crystalline I forms.

6. LINEAR EXPANSION OF RUBBER

Measurements of the linear expansion of rubber were made[9] to afford an independent check on the results of volume measurements, and to extend the observations to temperatures below those at which the ordinary confining liquids could be used. The specimen employed was in the form of a rod about 11 cm in length and 1.5 cm in

[9] The author wishes to thank Dr. Peter Hidnert of this Bureau for cooperation in making these measurements.

diameter. Measurements of the change in length were made with a dial gage graduated to 0.01 mm, using the quartz tube apparatus referred to above. Observations were made on the sample first in the amorphous form and then after it had been converted to the crystalline form. The results of the measurements are shown in figure 6 in terms of relative length plotted as a function of the temperature.

The observations on the sample in the amorphous form extended from the temperature of liquid air, or about −190 C, to about −72 C, above which temperature the sample decreased in length and gave indication that it was undergoing deformation under the pressure exerted by the measuring mechanism. In the crystalline form, however, it was found possible to observe the expansion from −190 to 0 C. No plastic deformation occurred, since at the end of the run the sample resumed its original length when replaced in liquid air.

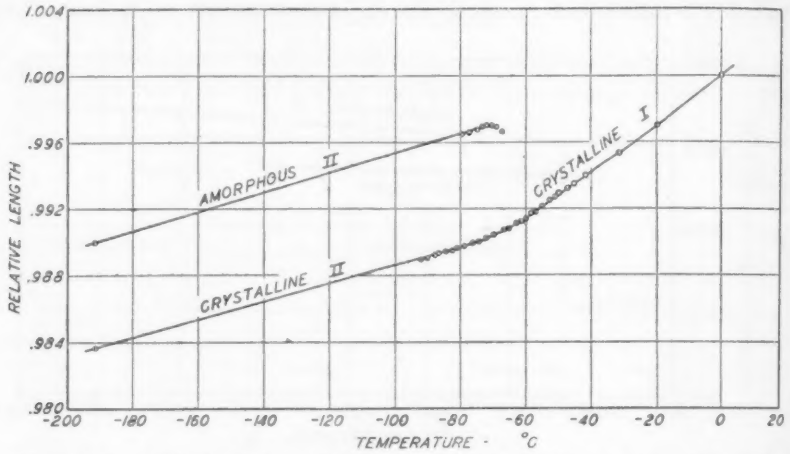

FIGURE 6.—*Relation between length of specimen of rubber hydrocarbon and temperature.*

Measurements on the amorphous II form were discontinued at about −70 C because of softening of the sample.

Relative positions of the curves for the amorphous and the crystalline forms in the figure were not found by direct observation but were computed from the change of volume on crystallization as measured with the dilatometer.

The curve for the crystalline form gives an indication of a transition in the neighborhood of −70 C, thus substantiating the results obtained with the dilatometers in which alcohol was used as a confining liquid.

The average linear coefficient of expansion for the amorphous II form between −190 and −72 C was 0.000060, while that for the crystalline II form was 0.000054. The volume coefficients which may be derived from these linear coefficients, assuming the rubber to be isotropic, are 0.00018, and 0.00016, respectively. These values are consistent with the value 0.00020 obtained from the dilatometer measurements between −85 and −72 C. They are slightly lower since they refer to a lower mean temperature. In the case of nearly

all substances the coefficient of expansion decreases with decreasing temperature.

The average linear coefficient of expansion for the crystalline I form from −72 to 0 C was 0.00014; this corresponds to a volume coefficient of 0.00042, which is somewhat lower than the value 0.00053 obtained with the dilatometer. No definite explanation can be offered for this discrepancy but it is possible that the pressure exerted by the measuring mechanism prevented equal expansion in all directions.

V. RESULTS WITH VULCANIZED RUBBER

Temperature-volume measurements were made on vulcanized rubber from −85 to +85 C and showed only one anomaly, which was comparable to the transition occurring at −72 C with the unvulcanized rubber. This anomaly was a change in coefficient of expansion, and with different compounds occurred at temperatures determined by the percentage of combined sulphur. Analogous to the nomenclature for unvulcanized rubber, the ordinary vulcanized rubber is called the amorphous I form and that having the low coefficient of expansion the amorphous II form.

The measurements on the vulcanized samples were made with dilatometers having capillary tubes of such capacity that a range of about 40 degrees centigrade could be covered by a continuous series of observations. The results are, therefore, somewhat less precise than those obtained with unvulcanized rubber.

The relative volumes of the samples are shown in figure 7 as a function of the temperature. In the case of each of the three compositions the relation to temperature is linear and is characterized by an abrupt change of slope. For the sample containing 2 percent of combined sulphur this change occurs at about −72 C; for 4 percent it occurs at about −62 C; and for 6 percent at about −53 C. The data are not sufficiently precise to give exact values for the coefficient of expansion. Within experimental error the coefficients of expansion above the transition points are the same and are about 0.00065; below the transitions they are all about 0.00022.

VI. DISCUSSION

The crystallization of rubber is essentially the same as the crystallization of any organic substance of high molecular weight. It is a relatively slow process and is speeded up by a certain degree of supercooling. Cooling quickly to a temperature considerably below the transition point, however, inhibits crystallization, presumably for the reason that the viscosity of the rubber becomes so great that the molecular orientation cannot take place to any appreciable extent. This is comparable to the supercooling and formation of glassy modifications by many substances.

In contrast to the behavior of unvulcanized rubber, vulcanized rubber, unless external force is applied, undergoes no volume change which might be attributed to crystallization at any temperature in the range covered by the investigation. This may be explained by assuming that in unvulcanized rubber the molecules have a sufficient degree of mobility to permit the formation of crystals, while in vul-

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canized rubber the molecules are linked together with sulphur or are so held by other forces that orientation to the extent necessary for the crystallization cannot take place spontaneously. There is, however, ample evidence that the application of external force may produce crystallization. The formation of X-ray diffraction patterns in stretched rubber is one type of evidence, while the change in volume of

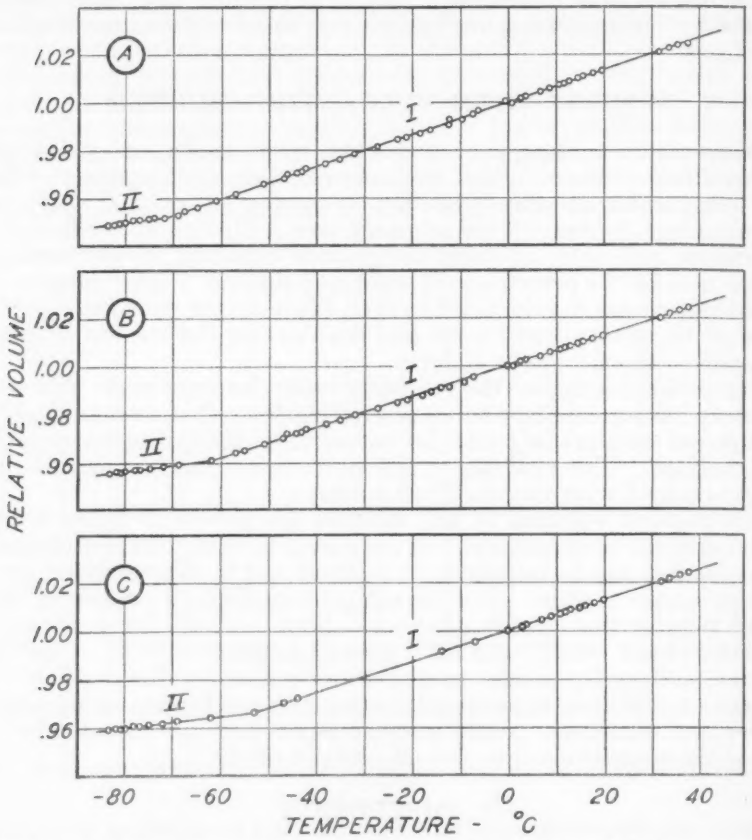

FIGURE 7.—*Relation between volume of rubber-sulphur compounds and temperature.*

Curve A refers to a compound with 2 percent sulphur, curve B to a compound with 4 percent, and curve C to a compound with 6 percent. I and II refer to the amorphous I and amorphous II forms, respectively.

rubber after stretching is another. This matter will be discussed further in a subsequent section of this paper.

The low temperature transitions which are observed to occur in both forms of the unvulcanized rubber and in the amorphous form of the vulcanized rubber are of the type considered by Ehrenfest [10] as transitions of the second order. In these transitions ΔS and ΔV are zero at constant temperature, but $\Delta\frac{dS}{dT}$ and $\Delta\frac{dV}{dT}$ are not zero; S being the entropy, V the volume, and T the temperature.

[10] Koninklijke Akad. Wetenschappen Amsterdam **36**, 153(1933).

Transitions of the second order are considered to arise from changes which take place within the molecule, such as excitation by rotation or vibration, in contrast to transitions of the first order which are associated with molecular phenomena, such as crystallization or changes of crystal structure. From this standpoint it is reasonable that the transitions from form I to form II for both the amorphous and the crystalline rubber should occur in the same temperature range, since the two forms are probably the same as regards the internal structure of the molecules.

The transitions from form I to II for the vulcanized rubber were observed to occur at temperatures which are determined by the percentage of sulphur in combination with the rubber. This is in accord with the well-established principle of organic chemistry that the addition of an atom or radical to a long chain molecule affects the properties not merely of the atom or groups to which the addition is made but also of remote parts of the molecule. Consequently, it is reasonable that the temperature at which the transition occurs should be changed by the addition of even a relatively small proportion of sulphur.

The crystallization of unvulcanized rubber is not sharp but takes place over the range 6 to 16 C. This fact indicates that the material dealt with is not a single definite molecular species but is a mixture of two or more kinds of molecules. The data here presented, however, are not adequate to warrant any speculation as to the number of types of molecules involved.

The present investigation does not afford a complete description of the forms of rubber because it does not include the well-known form of frozen rubber which undergoes transition to the amorphous form at about 35 C. The investigation of this form of rubber is in progress but the indications are that a long time, perhaps years, may be required for an adequate study since the transformation from the amorphous form to this crystalline form is very slow.

VII. COMPARISON WITH OTHER INVESTIGATIONS

The results of the present investigation serve to clarify and coordinate a variety of different observations that have been made regarding the influence of temperature on the properties of rubber. The measurements here reported for the transitions and for volume changes associated with the transitions are in agreement with some of the determinations by previous investigators which are summarized in table 2. The existence of rubber in different forms has a direct bearing on phenomena as diverse as the behavior of rubber on stretching and the change of electrical properties with temperature.

TABLE 2.—*Comparison of the data of different investigators on the crystallization of rubber*

Investigators	Type of measurement	Kind of rubber	Temperature of melting	Volume change
Bunschoten	Density	Raw	About 35 C after storage for several years in the frozen condition.	2.0 percent at 35 C.
Ruhemann and Simon.	Volume change in dilatometer.	Smoked sheet	About 8 C	Qualitative observations only.
van Rossem and Lotichius.	Hardness	Latex sheets	2 to 15 C	
Do	Density	do	do	2.5 percent at 0 C.
Do	do	do	About 35 C after storage for several years in the frozen condition.	3.1 percent at 35 C.
Carson	Manual examination	Milled crude	Below room temperature after storage for several months at 0 C; between room temperature and 50 C after similar storage under pressure.	
Smith, Saylor, and Wing.	Observations on crystals under polarizing microscope.	Pure ether-soluble fraction.	8 to 11 C depending on conditions of measurement.	
Gibbons, Gerke, and Tingey.	"T-50" test	Smoked sheet	16 C	
Present author	Heat capacity	Rubber hydrocarbon.	6 to 16 C	
Do	Volume change in dilatometer.	Rubber hydrocarbon and smoked sheet.	do	2.65 percent at 0 C.

1. FREEZING OF RUBBER

The work of previous investigators points to the existence of two forms of frozen rubber; one, the form melting at about 35 C, and the other, a form which may be identified with the one here designated as crystalline I. van Rossem and Lotichius [11] obtained the first of these by keeping rubber at a low temperature for several years, and the second by keeping rubber at a temperature of 4 C for about 10 days, or at −10 C for 3 or 4 days. The conditions under which the latter product was obtained were comparable to those found in the present investigation for producing the crystalline I form. The temperature range of transition to the amorphous form was 2 to 15 C which is roughly the same as the range 6 to 16 C found for the crystalline I form.

Carson [12] observed both types of freezing in crude rubber which had been kept in storage for 9 months. Samples which had been under an applied pressure were found to thaw at a temperature between that of room and 50 C, while the samples to which no pressure had been applied thawed at a temperature below that of room. The first of these may be identified with the form melting at about 35 C, and the second with the crystalline I form.

Recently Smith [13] and coworkers, at this Bureau, measured the properties of crystals of the pure ether-soluble fraction of rubber hydrocarbon. Their product was designated as true crystals to distinguish it from frozen rubber in which the individual crystals are not discrete. The true crystals melted sharply at temperatures which varied from 8 to 11 C with the conditions under which the determina-

[11] Kautschuk **5**,2(1929). Also Rubber Chem. Tech.**2**,378(1929). Cf. India Rubber J.**67**,69(1924).
[12] Ind. Eng. Chem. **23**,691(1931). Also Rubber Chem. Tech.**4**,417(1931).
[13] See footnote 8 for reference.

tions were made. These temperatures lie within the range found in the present investigation for the crystalline I—amorphous I transition, and it is probable that the product represents a single molecular species which is one of the constituents of the rubber used by the present and other investigators.

The volume change on crystallization was investigated by Bunschoten [14] who found a change of 2.0 percent for the transition at 35 C. van Rossem and Lotichius, however, found a change of about 3.1 percent for this transition at 35 C, and a change of about 2.5 percent for the transition from the amorphous I to the crystalline I form at a temperature of 0 C. The latter determination is in fair agreement with the average value, 2.65 percent, found in the present investigation.

Ruhemann and Simon [15] made some observations on the behavior of crude rubber in a dilatometer with mercury as a confining liquid. The curve which they obtained for the temperature-volume relation was but semi-quantitative, and showed a deviation from a straight line from about −25 to +10 C for which they offered no explanation. From the present results, however, it appears that when the sample was cooled to a low temperature it remained in the amorphous form at the lower temperatures, but when it was warmed slowly partial transition to the crystalline phase took place through the range −25 to +10 C with a resulting deviation from a straight line in the temperature-volume curve. At about 10 C the sample returned to its original amorphous condition, and the temperature-volume relation was again represented by a straight line.

Katz and Bing [16] studied the X-ray diffraction patterns of frozen rubber and concluded that it was crystalline, the crystals being in random orientation rather than in definite alignment as in stretched rubber.

Pummerer and Von Susich [17] sought, by means of X-ray diffraction studies, for evidence of crystallization in rubber that had been kept at −190 C for 8 days, but found none. This negative result is easily understood from the results of the present investigation which show that crystallization takes place readily only in the range from about +11 to −35 C, while at much lower temperatures the rate becomes so slow as to be inappreciable.

Unpublished work by the present author on the measurement of heat capacities of rubber indicates a transition of the first order in the vicinity of 10 C which is consistent with other findings of the present investigation. Ruhemann and Simon,[18] however, found a large latent heat effect at a temperature of 0 C. No interpretation for this latter observation can be offered at the present time.

2. CRYSTALLIZATION OF RUBBER BY STRETCHING

Several lines of evidence indicate that the crystallization of rubber which is brought about by stretching is closely allied to, if not identical with, the crystallization produced by freezing. Katz and Bing found, as was mentioned above, that the X-ray diffraction patterns of frozen rubber and of stretched rubber were identical except that the crystals

[14] Meded. Rikjsvoorlichtingsdienst behoeve rubberhandel rubbernijverheid, Delft, [3],37(1921).
[15] Z. phys. Chem. **138A**,1(1928).
[16] Z. angewandte Chem. **38**,439(1925).
[17] Kautschuk **7**,117(1931). Also Rubber Chem. Tech. **5**,245(1932).
[18] See footnote 15.

in the frozen rubber were in random orientation. Davey and his coworkers [19] showed that a small interval of time elapses between the extension of a sample of rubber and the appearance of an X-ray diffraction pattern. A similar time lag was recently observed in connection with the decrease in volume of rubber on stretching.[20] Measurement of the change in volume was found to afford a simple means for following the progress of crystallization. Under some circumstances a considerable part of the volume change occurred within a few seconds after the stretching, while under other circumstances a similar change required hours. This is further evidence that the rubber molecules do not form a crystal lattice in the process of stretching, but that crystallization is a subsequent and distinct process.

The melting of unvulcanized rubber which has been crystallized by stretching occurs in the same range of temperature as that of rubber crystallized by cooling. This is indicated by a comparison of the results of the "*T*–50" test described by Gibbons, Gerke, and Tingey [21] with measurements made in the present investigation. In the *T*–50 test rubber which has been stretched and cooled quickly is released and allowed to warm, observations being made on the temperature at which the rubber retracts to 50 percent of the original elongation. The above-mentioned investigators found a retraction temperature of 16 C for smoked sheet which had been stretched to 700 percent elongation. This corresponds to the higher temperature of the melting range, 6 to 16 C, reported in a previous section of this paper. This agreement is as would be expected since the restoring forces in stretched crystalline rubber would become operative only after much of the crystal structure had disappeared.

Measurements of the change in volume of rubber under conditions comparable to the T–50 test afford further evidence that the crystallization produced by stretching is comparable to that brought about by cooling alone. The results of one experiment [22] in this connection are shown in figure 8. In this experiment rubber rings cut from lightly-milled pale crepe were stretched to an elongation of about 350 percent, and cooled at once to a temperature of about 1 C at which they were kept for 19 hours. The volume decreased rapidly at first, and then more slowly. The magnitude of the change which took place is indicated by the curve AB. The rings were then released and allowed to warm slowly, and the increase in volume observed, the results being given by curve BCD. Although released, the rubber remained in its elongated form until a temperature of about 10.5 C was reached at which contraction in length began. At 12 C it had contracted to 50 percent of its elongation in the stretched condition, but recovery was not complete until a temperature of 24 C had been reached. The rubber samples were again cooled to a temperature of 1 C and measurements made as indicated by curve DA to complete the cycle.

The volume change on crystallization here observed was only 1.86 percent as compared with 2.20 percent for the crystallization of smoked sheet rubber by cooling alone. In another experiment, however, a volume change of 2.54 percent was observed when rubber produced

[19] Ind. Eng. Chem. **24**,54(1932). Also Ind. Eng. Chem. **26**,543(1934).
[20] Technical News Bulletin of the Bureau of Standards, 6, January 1934.
[21] Ind. Eng. Chem., Anal. Ed. **5**,279(1933).
[22] A. T. McPherson, unpublished work.

by the evaporation of latex was stretched to an elongation of 500 percent and kept at a temperature of 1 C for 8 hours. The point of inflection of curve BD is at 11 C which is in agreement with the midpoint of the melting range found for rubber crystallized by cooling alone.

The temperature at which rubber becomes brittle when cooled and bent quickly has been investigated by Kohman and Peek [23] who have found that the temperature is definite, and within limits is practically independent of the dimensions of the sample or the angle of bending. The temperature found for pale crepe was −58 C and for smoked sheet −57 C. These temperatures bear no apparent relation to any

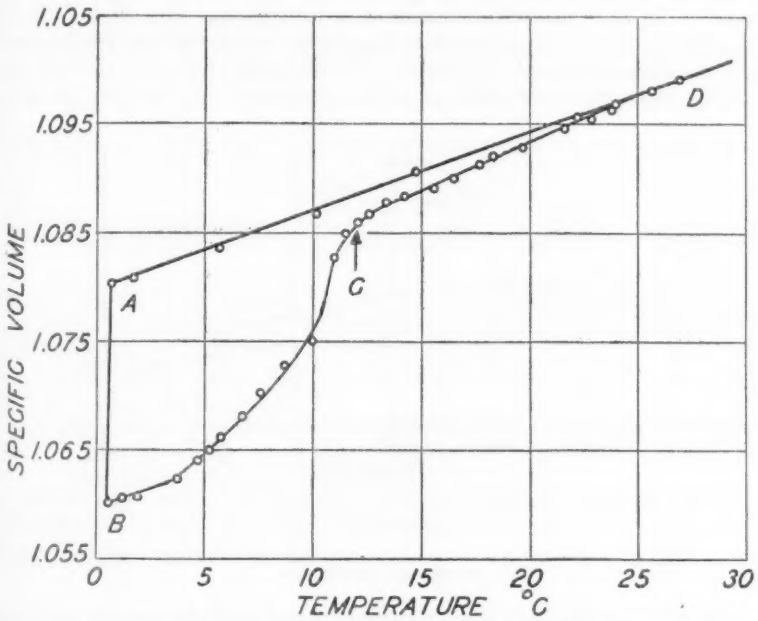

FIGURE 8.—*Temperature-volume relations of stretched and unstretched rubber.*

At A rubber is stretched; from A to B transition from amorphous to crystalline form occurs; at B rubber is released; between B and D rubber is allowed to warm, retraction being one-half complete at C; from D to A rubber is cooled to complete cycle.

of the changes in form which have been observed in the present investigation.

3. TRANSITIONS OF THE SECOND ORDER IN RUBBER

Ruhemann and Simon [24] found that unvulcanized rubber underwent a change in heat capacity at about −70 C. No latent heat effect was observed in connection with this transition, hence it is not a transition of the first order. Unpublished heat capacity measurements by the present author confirm the observations of Ruhemann and Simon as to the nature of this transition and the approximate temperature at which it occurs.

[23] Ind. Eng. Chem. **20,** 81(1928).
[24] See footnote 15.

Kimura and Namikawa [25] studied the specific gravity of rubber-sulphur compounds at different temperatures and found that these compounds underwent changes in coefficient of expansion at temperatures which were determined by the percentage of sulphur. The temperatures of transition observed for the compounds containing 2, 4, and 6 percent of sulphur, respectively, in the present investigation are in agreement with values taken from a curve published by them.

4. ELECTRICAL PROPERTIES OF RUBBER

Evidence for the changes in the form of rubber can be deduced from the results of a recent investigation on the electrical properties of rubber.[26] In this investigation it was found that the dielectric constant of the unvulcanized rubber was independent of the frequency at which the measurement was made. This being the case, the measurements of dielectric constants at all frequencies reported in the above-

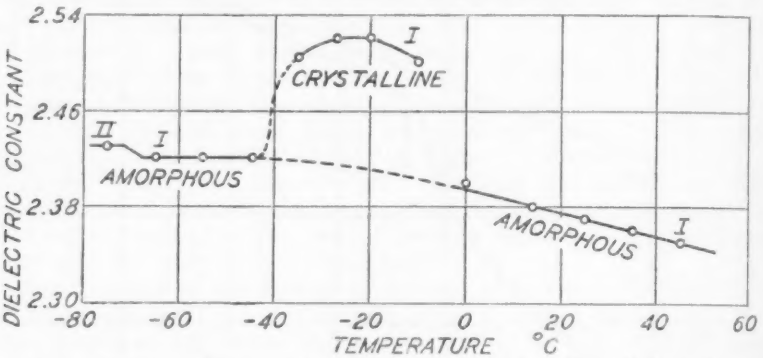

FIGURE 9.—*Relation between dielectric constant of rubber hydrocarbon and temperature.*

The data are from the paper referred to in footnote 26. The forms of rubber shown are those indicated by the present investigation.

mentioned investigation have been averaged and the results are shown in figure 9 for temperatures from −75 to +50 C. The prominent feature of fhe curve in this figure is the group of high values for dielectric constant between the temperatures of −35 and −10 C. These are about 0.1 unit above a smooth curve drawn through points for other temperatures, and on the basis of the present investigation may be attributed to the crystallization of rubber. The samples on which these measurements were made were first cooled to −75 C. and observations then taken at intervals of about 10° C while the temperature was slowly rising.[27] Between −45 and −35 C crystallization evidently took place and the values from −35 to −10 C pertain to the crystalline rather than to the amorphous form of rubber. One effect of the crystallization would be to change the dimensions of the specimens and make the observed dielectric constant values too high by about 0.05 unit. Taking a correction for this into consideration, the dielectric constant of the crystalline form of rubber is about 0.05 unit higher than that of the amorphous form.

[25] J. Soc. Chem. Ind. (Japan), Supplemental Binding **32**, 196B(1929).
[26] A. H. Scott, A. T. McPherson, and Harvey L. Curtis, BS J. Research **11**,173 (1933), RP585.
[27] Private communication from the authors.

This series of observations was discontinued at −10 C and a new series was made from 0 C to higher temperatures in which the samples were first cooled from room temperature to 0 C in about 1 day. Probably a little crystallization took place, causing the value for the dielectric constant at 0 C to be a little greater than that represented by the smooth curve.

Careful examination of the dielectric constant data in the low temperature range indicates by the change in slope of the curve a slight but definite anomaly between −75 and −65 C. Dielectric constant

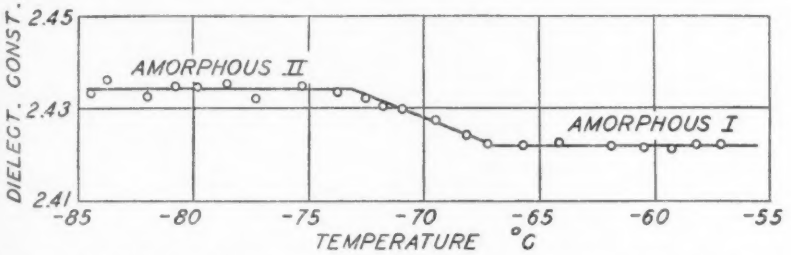

FIGURE 10.—*Relation between dielectric constant of rubber hydrocarbon and temperature showing transition between amorphous I and amorphous II forms.*

measurements were repeated at intervals of about a degree from −80 to −60 C.[28] The results of these measurements which are given in figure 10 show a transition between −73 and −67 C. This transition may be identified with the one in which form I of the amorphous rubber changes to form II.

The values for the dielectric constant given in the figure were corrected for temperature using the coefficient of expansion 0.00022 below −72 C and 0.00060 above this temperature.

WASHINGTON, July 24, 1934.

[28] A. H. Scott and A. D. Cummings, unpublished work.